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SOLUBILITIES OF BASES AND SALTS IN WATER AT 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	$0.0_{3}16$ $0.0_{4}10$	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	$0.0_{3}1$ $0.0_{4}6$	0.04 $0.0_{3}15$	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	$0.0_{3}35$ $0.0_{3}1$	0.006 $0.0_{3}17$	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 $0.0_{3}2$
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 $0.0_{3}92$	0.012 0.001	0.0016 $0.0_{3}2$	0.0076 $0.0_{3}14$	0.005 $0.0_{3}5$	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.36	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 $0.0_{3}14$	0.059 $0.0_{3}16$	0.05 0.001	0.25 $0.0_{3}57$	0.25 0.005	6.87 0.26	0.83 0.02	0.002 $0.0_{4}3$
OH	142.9 18	116.4 21.	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 $0.0_{3}2$	$0.0_{3}5$ $0.0_{4}5$	0.01 $0.0_{4}4$
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	$0.0_{3}23$ $0.0_{4}10$	0.011 $0.0_{4}6$	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 $0.0_{3}13$
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 $0.0_{3}15$	0.006 $0.0_{3}1$	$0.0_{3}38$ $0.0_{4}15$	0.12 0.006	0.4 0.03	73.0 4.3	. . . . . .	$0.0_{4}2$ $0.0_{3}5$
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0885 $0.0_{3}2$	1.48 0.030	0.0086 $0.0_{3}38$	0.0046 $0.0_{3}26$	$0.0_{3}56$ $0.0_{4}43$	0.03 0.0027	$0.0_{3}6$ $0.0_{4}4$	$0.0_{3}15$ $0.0_{4}5$
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 $0.0_{3}1$	4.95 0.10	0.0023 0.011	0.0011 $0.0_{4}7$	0.0013 $0.0_{4}13$	0.1 0.01	0.0042 $0.0_{3}32$	$0.0_{3}1$ $0.0_{4}3$

The ***upper number*** in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The ***lower number*** is the molar solubility, i.e., the number of moles contained in one liter of the saturated solution. The numbers for small solubilities have been abbreviated.

For some ***other solubilities***, see page 104.

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GENERAL CHEMISTRY FOR COLLEGES

BY

ALEXANDER SMITH

PROFESSOR OF CHEMISTRY AND DIRECTOR OF GENERAL AND PHYSICAL CHEMISTRY
IN THE UNIVERSITY OF CHICAGO

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PREFACE.

THE present work differs from the Author's "Introduction to General Inorganic Chemistry" in being intended for pupils who can devote less time to the study of the science, and whose needs can be satisfied by a less extensive course. It resembles the larger work in the arrangement of the contents and in the general method of treatment. The matter, and particularly the theoretical matter, however, has been simplified and has been confined strictly to the most fundamental topics. Such parts of the theory as are thus given, are presented with the same fullness as before, and are illustrated and applied with all the persistence needed to insure full apprehension and, ultimately, spontaneous employment by the student. Such parts as could not be treated in this way, within the limits set by the plan of the book, have been omitted. Methods materially different from those used in the "Introduction" have been employed in presenting many topics. Conspicuous differences of this kind will be noted particularly in the treatment of combining proportions, formulæ and equations, molecular and atomic weights, chemical equilibrium, ionic substances and their interactions, and the theory of precipitation.

The writer desires to express his profound gratitude to the many chemists who have made valuable criticisms and suggestions. Most of these comments applied to the "Introduction to General Inorganic Chemistry," but many of them have been used in preparing this work (General Chemistry for Colleges), and all will be considered in the second edition of the larger book.

For critical reading of the whole of the proofs of the present work, the writer desires especially to thank Messrs. A. T. McLeod and Alan W. C. Menzies of the University of Chicago. Other corrections and suggestions will be gladly received by the author.

ALEXANDER SMITH.

CHICAGO, April, 1908.

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* The titles of most of the descriptive paragraphs have been omitted from this table because it is easier to find matters of this nature by consulting the index. The titles of all the theoretical paragraphs, however, have been included.

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GENERAL CHEMISTRY FOR COLLEGES

GENERAL CHEMISTRY FOR COLLEGES

CHAPTER I

INTRODUCTORY I

As human knowledge has increased, it has become necessary to subdivide into groups the growing accumulation of truths, and to do this in a somewhat arbitrary fashion. Each such group is called a **science**, and includes a more or less distinct body of knowledge. That the boundaries of these groups do not exist in the subject-matter itself is seen at once in our own treatment of them. Thus, for convenience, we include in the science of physiology the study of the way in which the parts *of both plants and animals* perform their functions. The sciences, therefore, are not mutually exclusive, and their boundaries overlap in every direction. The difficulty in deciding what are the most convenient boundaries is as great with chemistry as with the other groups. In particular, the line which divides physics and chemistry from one another is often difficult to draw. It is assumed, however, that the reader is already familiar with the elements of physics, and so, in place of entering upon an academic discussion of the nature of this line, we shall allow its location to emerge as we proceed.

The same principle of grouping is pursued within each field. Thus the preparation and properties of chemical compounds is called *descriptive* chemistry. Again, the means that have been devised for recognizing the components of mixtures or compounds and measuring their quantities constitute the several branches of *analysis*. The subdivisions of chemistry of this kind are numerous.

The ideal in view in thus classifying the content of a science is to convert it into an **organized body of knowledge**. The various ways used to organize the facts of a science will be presented in detail as opportunity offers. These ways constitute what is called the **scientific method**.

Chemical Phenomena: Their Most Obvious Characteristic. — Chemistry being primarily an experimental science, we can best make our first approach to it through the consideration of some familiar chemical phenomena which shall serve as illustrations.

When clean iron is exposed to air and moisture it becomes rusty, first on the surface, and finally throughout its whole mass. The iron with which we start is a dark-gray, metallic-looking substance, which has a high specific gravity (about 7.5), is ductile, has great tenacity, and is readily attracted by a magnet. Rust, on the other hand, is a reddish or brownish substance which has an earthy appearance, is much lighter specifically than iron (sp. gr. about 4.5), is brittle, and is not attracted by a magnet. The phenomenon seems to have consisted in the gradual substitution of the second of these substances for the first.

The *chemical fact* here is that iron, when in contact with air and moisture, gives rust. Consideration will show, however, that we do not perceive this fact except by noting the *physical qualities* of the original and of the final materials. The data describing a chemical phenomenon consist in an enumeration of physical observations, like the above physical properties of iron and rust. It is, indeed, an invariable characteristic of every chemical phenomenon that our information is all derived from physical study of the materials. Thus, when a candle burns, it undergoes a chemical change, and we observe a solid, waxy substance disappearing progressively from view. A closer study of the facts shows that a mixture of gases is rising from the flame, and we find that the material of the candle is contained in this. Here, again, we use physical means of observation.

It is further true of these, as of all chemical phenomena, that the *physical properties* of the original and those of the final substances *are invariably entirely different.* We observe also that this sort of transformation is *always abrupt.* As the change spreads, the minute fragment of iron of one moment becomes the minute fragment of rust of the next, and is endowed at once with all the new properties in full measure. No part of the mass loses its magnetic qualities completely, for example, before it has reached the limit of change in color or tenacity. Since we are compelled to define the species of matter by their constant physical properties (see pp. 20, 23), the possession by two or more bodies of permanently different properties

constitutes them *ipso facto* samples of different materials. We may, therefore, say, more briefly, that the products of a chemical change are recognized at once to be *new and different substances.*

Thus the **most obvious characteristic** of a chemical phenomenon is: **that all the physical properties of the substances alter; that this alteration is abrupt, so that, in fact, the products are different substances; and that the recognition and study of such a phenomenon is accomplished entirely by observations of a physical nature.** Other characteristics, less obvious, but equally constant, will presently be brought to light.

The chemical phenomena which are familiar are innumerable. The burning of illuminating-gas, the coagulation of the white of an egg, the decay of animal and vegetable matter, the action of hard water on soap, and the slaking of quicklime, are examples. The reader should analyze these changes, applying the above criteria, and see for himself why they are classed as chemical.

So far as this first characteristic is concerned, some merely physical phenomena will be recalled, which are not unlike the rusting of iron. Thus, when water is raised in temperature, its properties begin to alter: it becomes more mobile, its specific gravity changes, its refracting power for light is modified, and so forth. At first, however, these changes proceed by imperceptible gradations and lack the abruptness of chemical change. But when 100° C. is reached the water passes into steam, and the whole of the properties of this gas are different from those of water. Conversely, by cooling, the water may be converted into ice, and again there is an abrupt and profound change in properties. On this account, some chemists classify "changes of state of aggregation" as chemical phenomena. More usually, however, ice, water, and steam are regarded as identical, and not different substances.

Fact and Generalization or Law. — If the preceding section be reëxamined, it will be seen that a number of **facts** are mentioned in it. We begin the organization of knowledge according to the scientific method by trying to determine the facts. Thus, we find some specimens of iron are variously colored, and some are brittle. Examination shows, however, that the former peculiarities are due to paint, for example, and the latter to the presence of carbon and other foreign materials in the iron (cast iron). Finally, we ascertain the facts that iron itself is gray and tough.

Putting together a statement like that appearing in heavy type above, is the second step. We examine facts of a like kind, or pertaining to like phenomena, to see whether any general statement can be made that will cover some feature common to the whole of them. In the above illustrations, after settling the intrinsic properties of several substances, and then determining the facts about the way in which these properties are affected under certain circumstances, we decide that, when all the properties change abruptly in a permanent way, the cases in which this takes place shall constitute a distinct class, and we call them cases of chemical change. The statement which, in a few words or phrases, sums up those features of all the phenomena of like kind which are constant, is called a **generalization.** Often it is called a **law**, and sometimes a **principle.** A **generalization** or **law** in chemistry, therefore, is a **brief statement describing some constant mode of behavior.** The most important laws, like that describing the behavior of gases when compressed (Boyle's law), are usually connected with the names of the men by whom the relationships were discovered and the generalizations formulated.

The Explanation of Rusting. — In considering the complete disguise which is assumed by a substance that has undergone a chemical change, like rusting, the first question which arises is: Can we in any way account for this great and permanent change in properties which very generally distinguishes the chemical phenomenon from the physical? Some additional facts will be required before we can answer this question. It has long been known that many metals besides iron undergo an alteration similar to rusting, and that, where the transformation does not occur spontaneously, heating prompts it. The first fact which seemed to throw light on the subject was the observation that a piece of metal becomes heavier when it rusts. This was noticed as early as 1630, by a French physician, Jean Rey. His work was done chiefly with lead and tin, the former of which gives a dirty yellow, and the latter, a white powder, on rusting. He inferred correctly from his experiments that contact with the air had something to do with this chemical change. Other investigations on the same subject were made by Boyle (1627–1691), Mayow (1645–1679), and Hooke (1635–1703), in England, and they led to the same conclusion. The

increase in weight was to be accounted for, therefore, by the supposition that some material from the air had been added to the metal during the process. In other words, iron, for example, was one substance composed of iron only, and rust was another substance composed of iron and some other material taken from the atmosphere; and, the two substances being different in composition, their properties might naturally be expected to differ. The substance taken from the air was subsequently named oxygen.

The fact that foreign matter was actually gained by a body during the process of rusting was not generally accepted, however, until it was demonstrated anew by Lavoisier (1774) a century and a half later. He showed that a portion of the air really disappeared when tin rusted, and that the increase in weight of the tin corresponded with the loss in matter of the air.

Explanation in Science. — The word **explanation**, which was employed repeatedly in the last section, is used in science as the name of a definite process. It stands simply for **a description in greater detail.** Thus, when, to the acquaintance with the outward manifestations of rusting, we are able to add the further description that it is produced by the union of oxygen from the air with iron, we feel increased satisfaction, and we say that an explanation has been found.

There is no such thing as a final explanation, however. At the very next step, when we ask why the union of oxygen and iron produces a body that is red and non-magnetic, we are compelled to say we do not know.

An explanation in science never professes for a moment to give the reasons for any occurrence. We simply do not know *why* behavior in nature is as it is.

Three Illustrative Chemical Phenomena. — Since oxygen is an invisible gas, the demonstration that rusting consists in the union of this gas with a metal, requires somewhat complicated apparatus. The next illustration, while lacking historical interest, is simpler, because both substances are visible, and are easily handled.

Iron unites, not only with oxygen from the air, but also, with almost equal ease, with sulphur. To study the behavior of the materials we must know their properties. The properties of iron

we have already enumerated (p. 2). Sulphur is a pale-yellow substance of low specific gravity (sp. gr. 2). It is easily melted (m.-p. 114.5° C.), and, although it does not dissolve in water, it may be dissolved completely in carbon disulphide. It crystallizes in rhombic forms (Fig. 1). Now, when iron filings and powdered sulphur are rubbed together in a mortar, the product, although it has a different color from either of the constiuents, is still really composed of the two original kinds of matter, side by side. With the help of a microscope and a needle, they can be picked apart completely. By manipulation of the mixture with a magnet, we may remove some of the iron without much difficulty.

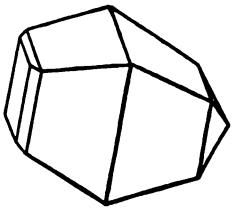

FIG. 1

Again, using the solubility of sulphur in carbon disulphide and the insolubility of iron, we may shake a portion of the mixture with this liquid in a test-tube, and so dissolve out the sulphur (Fig. 2). When the contents of the tube are poured on to a filter (Fig. 3), the liquid (the **filtrate**) runs through, carrying all dissolved matter with it, and leaving undissolved matter behind. The filtrate may be allowed to evaporate (Fig. 4), when yellow crystals of rhombic outline will be found to be the *sole residue*. The dark material remaining on the filter, when dry, is *wholly* attracted by a magnet. All these facts convince us that the properties of the components are still unaltered, and that, therefore, no chemical change has occurred.

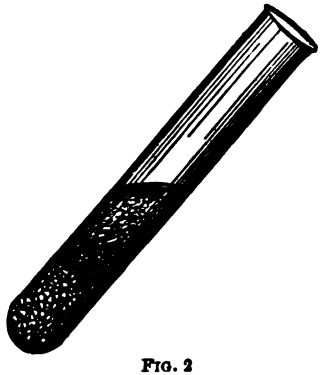

FIG. 2

If we now put some of the original mixture into a test-tube and warm it, we soon notice a rather violent development of heat taking place, the contents begin to glow, and what appears to be a form of combustion spreads through the mass. The heating employed at the start falls far short of accounting for the much greater heat produced. When these phenomena have ceased, and the test-tube has been allowed to cool, we find that it now contains a somewhat

porous-looking, black solid. This material is brittle; it is not magnetic; it does not dissolve in carbon disulphide; and close examination, even under a microscope, does not reveal the presence of different kinds of matter. This substance is known to chemists as ferrous sulphide, and, as we see, its properties are entirely different from those of the constituents.

A substance formed in this way by the union of other materials is called a **compound.** The rusts given by various metals are therefore compounds also.

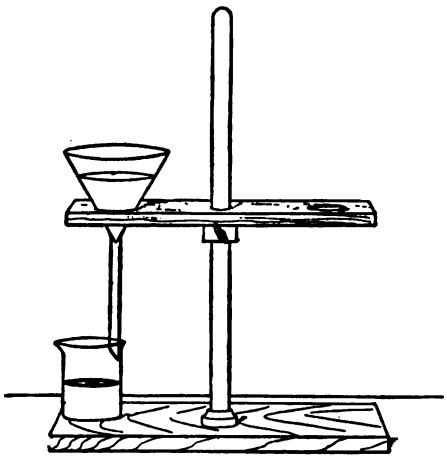

FIG. 3

The **second illustration** is selected on account of its historical interest. One of the earliest chemical changes in which a gas, recognized to be distinct from air, was observed among the products, was noticed by Priestley (1774). The observation was made with mercuric oxide, a bright red, rather heavy powder. When this substance is heated (Fig. 5), we find that a gas is given off, which is easily shown to be different from air, since a glowing splinter of wood is instantly relighted on being immersed in it. The gas is pure oxygen.* We notice also during the heating that a sort of mirror appears on the sides of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal mercury, or quicksilver. If the heating continues long enough, the whole of the red powder eventually disappears, and is converted into these products.

FIG. 4

The extensive nature of the change in properties in this case is

* Air (*q.v.*) is a mixture of which only one-fifth is oxygen.

evident. It should also be observed that continuous heating is required to maintain this change in operation. It differs markedly from the iron and sulphur case in this respect. When the flame is removed, the evolution of oxygen ceases. The significance of this will appear shortly.

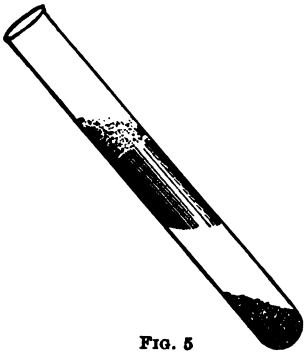

FIG. 5

The **third and last example** is taken purposely in order to illustrate the variety of ways in which chemical change may be carried out. It is the interaction of silver nitrate and sodium chloride (common salt). The substances may be recognized by the form of the crystals of which they consist. The latter is composed of small cubes (Fig. 6), while the former presents a less familiar form geometrically (Fig. 7). Both substances are capable of being dissolved in water and, for this experiment, portions of each substance are shaken in separate vessels with water, until none of the solid remains. When the solutions are now poured together, we observe that the clear liquids at once become opaque, and that a dense mass of white, solid material appears suspended in the mixture (Fig. 8). This white substance consists of an extremely fine powder without any observable crystalline form. We know at once that it must represent a new substance, since it would not have appeared had it been soluble in water like the two materials from which it was made. We continue adding the one liquid gradually to the other until no further formation of this solid takes place, and then stop. By filtration (Fig. 3), we obtain the insoluble material (the **precipitate**) upon the filter paper, and the clear liquid (the **filtrate**) passes through and is caught in the vessel below.

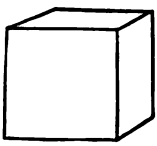

FIG. 6

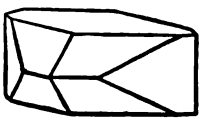

FIG. 7

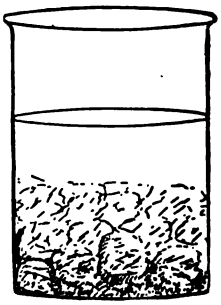

FIG. 8

We are confronted with two possibilities: either both the original

materials have come together to form *one* white insoluble material, or some other product (or products) may be present in addition to it. In the latter case, search must evidently be made in the liquid. By evaporating the *filtrate* in a suitable vessel (Fig. 4), we find that the second assumption represents the fact, for a considerable quantity of a white crystalline substance remains. The homogeneous character of this shows that there was but one product in solution, while the same property of the precipitate shows that there are but two products altogether.

The insoluble material is composed of silver and chlorine, and it is known as silver chloride. Like some other compounds of silver, it darkens on exposure to light, turning first purple and then brown, and being decomposed by this agency into its constituents. The chlorine, a gas, escapes, and a brown powder consisting of finely divided silver remains. The soluble solid obtained from the filtrate, we recognize as identical with a mineral, sodium nitrate, which is found in Peru. Its crystals are rhombohedral (Fig. 9). They resemble cubes which have been slightly distorted by pressing inwards two opposite corners. This change presents several features which distinguish it from the previous ones: it is much more complex; it takes place in the presence of water; it requires no heating for its promotion; and the change is complete the instant the materials have been mixed, while the others required a good deal of time for their accomplishment.

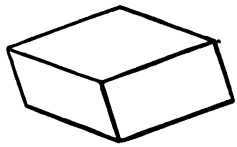

FIG. 9

The Kinds of Chemical Change. — Having these three cases before us, — and they are types of most chemical phenomena, — we now proceed to analyze them, and so take another step towards explaining (*i.e.*, describing in detail) the nature of a chemical phenomenon. In the iron and sulphur experiment (p. 6), two materials were used, and a different one with new properties was produced. Here, in chemical language, the first two substances **united** or underwent **combination**:*

Iron + Sulphur *gave* Ferrous sulphide.

The rusting of iron, lead, and tin belongs also to this class. In the second illustration (p. 7), one material was used, and it was driven

* The word **mixed** is used only of substances which are mingled, physically, and not combined.

apart by heating so that two new ones arose. A chemical phenomenon of this kind is called a **decomposition**:

Mercuric oxide *gave* Mercury + Oxygen.

The last was the most complex. The substances, with the constituents of each, were as follows:

Silver nitrate + Sodium Chloride *gave* Silver Chloride + Sodium nitrate.
(Silver, nitrogen, oxygen) (Sodium, chlorine) (Silver, chlorine) (Sodium, nitrogen, oxygen)

Here the constituents of both the ingredients became separated (decomposition), and the products of decomposition mated themselves differently (combination). Thus, for example, the silver of one ingredient combined with the chlorine of the other. A third variety of chemical change consists, therefore, in the **concurrence of both of the first two kinds** in the same action. As several different varieties of this sort of complex redistribution of material can be distinguished, a distinct name is given to each. The present is called a **double decomposition.**

When we encounter other chemical changes, we shall find the extent of the stride we have taken in this critical analysis of a few examples. It will then appear that there are only a few changes which cannot be placed in one of these three categories, and these all belong to a fourth class. It occasionally happens, especially in the case of compounds of carbon, that one single kind of material turns into another single kind of material. Nothing is added and nothing removed, yet the new substance has different properties in every respect from the old. Most of those substances whose transformation is definitely assigned to this class contain several constituents. Now, we have seen that when substances have different properties they differ also in their constituent materials. Carrying out this idea, the hypothesis (or suggestion) has been made that, since here also the properties change, there must be some readjustment of the material, even in cases like this. Hence, we designate changes of this kind **internal rearrangements.** The composition of the material is unaltered, so we suppose its constitution to have become different. If the chemists ever decide to regard the change of water into ice or steam as a chemical phenomenon, all changes of state of aggregation would be placed in this fourth class. It is here only that the boundary between physics and chemistry is at present difficult to define.

The Second Characteristic of Chemical Phenomena. — We are now able to make another generalization (or condensed statement of fact): **In chemical phenomena substances enter into combination, come out of combination, or change their associates in combination or their state in the compound.** In other words, **the material changes its composition or its constitution.**

This generalization furnishes an explanation of the former (p. 3) to a certain extent. Each individual substance has its own composition and its own set of physical properties. Hence, when, by chemical transformation, substances of new and different composition are produced, the materials must simultaneously acquire the specific properties of the new substances.

A chemical phenomenon is named an **action** or **interaction.** It is also often called a chemical **reaction.** Thus, we say that four classes of *reactions* have been described above.

Summary. — Thus far, we have learned that chemistry deals with the changes in composition and constitution which substances undergo, and with the alteration in properties which accompanies and gives evidence of those changes.

Exercises. — 1. Take one by one the words or phrases printed in black type and the titles of the sections in this chapter, and endeavor to recollect what you have read about each. In each case try, (*a*) to recall the meaning and to state it in your own words; (*b*) to recall the facts associated with, and the reasoning which led up to the point in question; (*c*) to recall examples illustrating the conception and to apply the conception in detail to each example. Whenever memory fails to give a perfectly clear report of the matter in hand, the text must be read and reread until the essential point can be repeated from memory.

Use the same method in all future chapters. A useful practice is to employ a pencil as you read and to underline systematically all the important facts and statements, and then to go back and apply to each marked place the process described above.

2. Define the following and state how each is measured: specific gravity, ductility, tenacity, brittleness.

3. Take the chemical phenomena mentioned on p. 3, par. 2, and enumerate the physical properties of the substances before and after the chemical change.

4. Define and illustrate: filtrate, mixture, compound, precipitate.

CHAPTER II

INTRODUCTORY II

If we now return to the three illustrations of chemical phenomena which we have been studying (pp. 5–9), we shall find a new question arising naturally out of them. This is, whether the *mass* of the materials is altered, as are the other attributes, in these chemical changes.

Third Characteristic of Chemical Phenomena: Conservation of Mass. — The most painstaking chemical work seems to show that, if all the substances concerned in the chemical change are weighed before and after the change, there is no evidence of any alteration in the quantity of matter. The two weights, representing the sums of the constituents and of the products respectively, are, indeed, never absolutely identical, but the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, as a **third characteristic** of all chemical phenomena, that **the mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the conservation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other properties, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations. This is the only attribute which persists.

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly the gradual disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we catch *the gases* which rise through the flame, we find that the gases weigh even more than the part of

the candle which has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels, which permit neither escape nor access of material, we find that the weight does not alter.

Physical Accompaniments of Chemical Change.—Study of the three typical chemical changes described in the last chapter may now be resumed, in order to see whether anything further of a general nature is characteristic of such phenomena. We recall at once that a prominent feature of the union of iron and sulphur was the **heat** which, as shown by the glow spreading through the mass, seemed to be developed after the action was once started. It is found that many chemical changes are like this one, in exhibiting simultaneously the production of very perceptible amounts of heat. On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 8), owed its continuance to the persistent application of heat, and ceased so soon as the source of heat was withdrawn. Here, apparently, heat was consumed during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of heat** may, therefore, be a feature of chemical change.

In the iron and sulphur case, as in other chemical actions where the heat developed is great, **light** also was given out. In the last of the three actions, on the other hand, we obtained a substance (silver chloride), which may be kept for any length of time in the dark, but, by the action of sunlight is broken up into its constituents (p. 9). It would appear, therefore, that **light may be given out or used** in connection with chemical change. Noting these facts stimulates us to look for other similar accompaniments of change in composition.

If we dip two wires from a battery or dynamo into a solution of nitrate of silver (Fig. 10), such as was used in the third experiment, we observe the instant production of a coating of silver on the negative wire. By preparing the solution properly and allowing the **electricity** to flow through it for a sufficient length of time, all of the compound can be decomposed and all its silver deposited. It is needless to say that this release of the silver from chemical combina-

tion, and liberation of the metal at the electrode, goes on only so long as the current of electricity is employed, and that electricity is consumed in the process. Very many substances can be decomposed in this way.

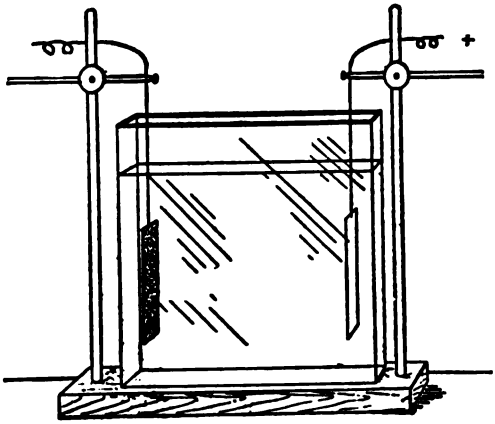

FIG. 10

The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc, we find that a gas is given off rapidly (Fig. 11), that the zinc gradually dissolves, and that a large amount of heat is developed. Under favorable circumstances, the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire, and, having provided a plate of platinum also connected with a wire, immerse the two simultaneously in the acid (Fig. 12), then a galvanometer, with which the wires are connected, shows at once the passage of a current of electricity round the circuit. Exactly the same chemical change goes on as before. The sole difference is that the gas appears to arise from the surface of the platinum. It is easy to show, however, that the platinum by itself is not acted upon by dilute acids, and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan produced, we get electricity. The arrangement is, in fact, a battery-cell, for a battery is a system in which a chemical action which would otherwise give heat furnishes electricity instead. Thus,

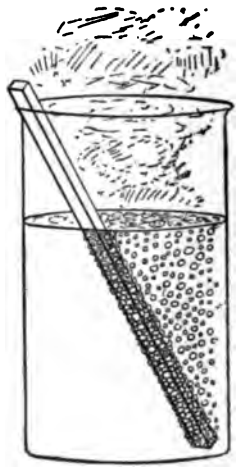

FIG. 11

electricity may be consumed or produced in connection with a change in composition.

Even violent rubbing in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes. In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance

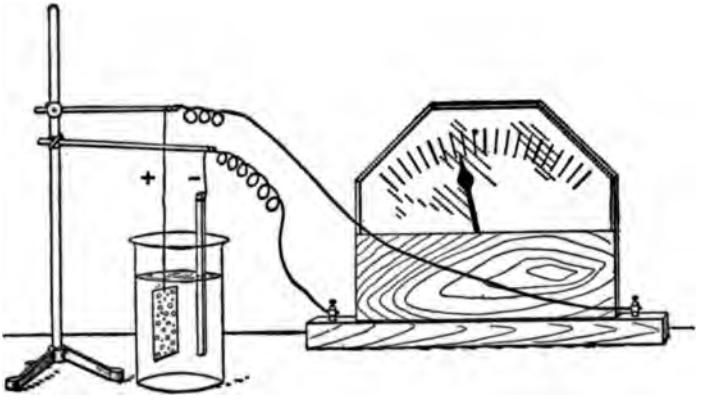

FIG. 12

appears as heat. Conversely, the *production* of mechanical energy, as the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced** in chemical changes.

Summing up our experience, we may state that no change in composition occurs without some accompaniments, such as the production or consumption of heat, light, electricity, or, in some cases, mechanical energy.

Classification of the Accompaniments of Change in Composition: Energy. — The problem of classifying (*i.e.*, placing in a suitable category) things like heat, light, and electricity has occupied much attention. They do not possess mass. In all changes in composition, one of these natural accompaniments is given out or absorbed, sometimes in great amount, yet, in none is any alteration in weight observed. There are many things which are real, how-

[illegible] affected by gravitation. In the present [illegible] as follows:

A [illegible] is different from a brick at rest. The former [illegible] that the latter cannot. Furthermore, we can [illegible] in our minds. The brick can be deprived of [illegible] with it again. Thus, we can get the idea [illegible] as a separate conception. Similarly, we observe that a [illegible] behaves differently when hot, and when cold, when [illegible] of electricity, and when bearing none. We con[illegible] the brick or the iron as having a certain amount and [illegible] which is unalterable, and as having motion, heat, or [illegible] added to this or removed. Thus, we describe our obser[illegible] two categories, one of which includes the various [illegible] matter, and the other, various things whose association with [illegible] seems to be invariable and is often so conspicuous.

At first sight, these accompaniments of matter seem to be quite unrelated. But a relation between them can be found. If the heat of a Bunsen flame or of the sun is brought under a hot-air motor (Fig. 13) violent motion results. Again, if the motor is connected with a dynamo, electricity may be generated. Still again, if the current flows through an incandescent lamp, heat and light are evolved. Conversely, when motion is impeded by a brake, heat appears. When a current of electricity is run through the dynamo, motion results. But the most significant facts are still to be mentioned. The heat absorbed by the motor is found to be greater when the machine is permitted to move and do work, than when it is not. Thus, it is found that when work is done some heat disappears, and this heat is, in fact, transformed into work. Similarly, when the poles of the dynamo are properly connected and electricity is being produced, and only then, motion is used up. This is shown by the effort required to turn the armature under these circumstances, and the ease with which it is turned when the circuit is

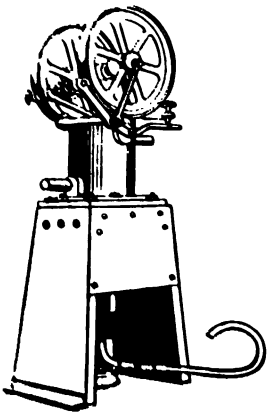

FIG. 13

open. So, with a conductor like the filament in the lamp, unless it offers resistance to the current and destroys a sufficient amount of electricity, it gives out neither light nor heat. Finally, motion gives no heat unless the brake is set, and effort is then demanded to maintain the motion. These experiences lead us to believe that we have here a set of things which are fundamentally of the same kind, for each form can be made from any of the others. We have, therefore, invented the conception of a single thing, of which heat, light, electricity, and motion are forms, and to it we give the name **energy: energy is work and every other thing which can arise from work and be converted into work** (Ostwald).

Closer study shows that equal amounts of electrical or mechanical energy always produce equal amounts of heat. There is never observed any loss in any of the transformations of energy any more than in the transformations of matter. Hence, J. R. Mayer (1842), Colding (1843), and Helmholtz (1847) were led independently to the conclusion that **in a limited system no gain or loss of energy is ever observed.** This brief statement of the results of many experiments is called the law of the **conservation of energy.**

Application of the Conception of Energy in Chemistry. — At first sight it looks as if the statement that energy is conserved is not applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or by the union of iron and sulphur in our first experiment? Since we do not perceive any electricity, light, heat, or motion, in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **internal energy.** Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as being stored in the products of decomposition in the form of internal energy.

These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter,

each of these constituents being equally real and equally important. A piece of the substance known as "iron" must thus be held to contain so much iron matter and so much internal energy. So ferrous sulphide contains sulphur matter, iron matter, and internal energy. Thus, by a *substance* we mean a distinct species of matter, simple or compound, with its appropriate proportion of internal energy.

In the course of this discussion it has become clear that a **fourth characteristic** of chemical phenomena is that, besides a change in the state of the *matter*, **there is always an alteration in the amount of internal energy in the system. This alteration consists in the production of internal energy from, or the transformation of internal energy into, an equivalent amount of some other form of energy.**

The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not employ zinc in batteries with the object of making zinc chloride or zinc sulphate. So we use the electrical energy, and throw the material products away when we refill the jars. It is the same with burning illuminating-gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery in order to make a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. In industry and life fully half the total amount of chemical change involved is set in motion by us, solely on account of the energy changes it involves. But the production of energy in chemical change is not only thus of practical importance; it is also of scientific interest, as will be seen in the next section.

Chemical Activity. — Other things being equal, actions in which there is a relatively large loss of internal energy proceed rapidly; that is to say, in them a large proportion of the material is changed in the unit of time. Those in which less energy is transformed proceed more slowly. The speed of the chemical change, and the quantity of energy available because of it, are closely related. Now, we are accustomed to speak of materials which, like iron and sulphur,

interact rapidly and with liberation of much energy as "chemically active." Thus, **relative chemical activity** may be estimated, (1) by observing the speed of a change (see Speed of chemical actions), or, in many cases (2) by measuring the heat developed (see Thermochemistry), or (3) by ascertaining the electromotive force of the current the change gives, when arranged in the form of a battery-cell.

It is evident that the chemical activity of a given substance will not be the same towards all others. Thus, iron unites much more vigorously with chlorine than with sulphur, and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, iron does not unite at all. One of the tasks of the chemist is to make such comparisons as this (see Specific chemical properties). Evidently, the substances containing the most chemical energy will be in general the most active.

The "Cause" of Chemical Activity. — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? The answer is that we do not know. Questions like this have to go without answer in all sciences. What is the cause of gravitation? We know the facts which are associated with the word — the fact that bodies fall towards the earth, for example — but why they fall we are unable to say. So, with chemical change, we can state all the facts we know about it, but even then we cannot say *why* it takes place.

The word **cause** was employed in the heading of this section, and it will be observed that no cause was found. This is the invariable rule in physical or chemical phenomena. We know of no causes, in the sense in which the word is commonly employed.

The word cause has only one definite use in science. When we find that thorough incorporation of the three materials is needed to secure good gunpowder, we say that the intimate mixing is a cause of its being highly explosive. By this we simply mean that intimate mixture is a *necessary antecedent* of the result. A **cause is a condition or occurrence which always precedes another condition or occurrence.**

Of Elements and of Simple and Compound Substances. — If we place before a physicist samples of iron, ferrous sulphide, and sulphur, he will report that there are three absolutely distinct *substances* represented, because they show three different sets of physical properties. A chemist, on the other hand, while admitting the accuracy of the report, in view of the criterion used by the physicist, which indeed he uses himself (*cf.* pp. 2-3), will insist on adding that there are only two perfectly distinct *kinds of matter* in the set, because he can make the second from matter furnished by the other two. In a sense, chemistry reduces the kinds of different matter to a much smaller number than does physics or any of the other sciences, and so it is the final authority in all questions involving matter. By the chemist, dozens of physically distinct substances are regarded as closely related because they all can be made with iron, or when decomposed give it; hundreds are alike in that sulphur enters into their composition; thousands are compounds of oxygen. In fact, the number of kinds of matter which are perfectly distinct in the strictly chemical point of view is quite limited.

The first to put our modern view into definite language was Lavoisier in his *Traité de Chimie* (1789). His work showed that decomposition had its limits. Mercuric oxide could be decomposed into mercury and oxygen, but no means was found of breaking these up in turn and producing any fresh substances from them. The kinds of matter composing these simple materials he named **elements.** The element is to be regarded as an ultimate chemical individual just as the substance is the physical individual. The definition of an element is therefore: **a distinct species of matter which has not been shown to be composite.**

The caution which prompted Lavoisier to use, as he did, the words " has not *yet* been," was justified by the fact that several substances, in his time regarded as elementary, were afterwards shown to be compound. Thus, quicklime was a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was a compound of this metal with oxygen. Discoveries similar to this have been made on more than one occasion since.

Until recently, a body made up of one or more specific elements had never been found to yield any simple substance different from those used in preparing it. In other words, one element had never been turned into another. The production of helium, neon, and

argon by the spontaneous decomposition of the radium (*q.v.*) emanation, and the formation of traces of lithium from copper sulphate, both observed recently (1907) by Sir William Ramsay, may lead, however, to a revision of the conception of an element.

We have seen (p. 18) that all substances, that is, physical individuals, must be thought of as containing matter and energy. We have now learned that there are two kinds of substances, namely, **compound substances** which **contain two or more elements together with the appropriate amount of energy**, and **simple substances** which **contain only one element together with a certain quantity of energy**. Among the substances which we have been handling, iron, sulphur, mercury, oxygen, and hydrogen are simple substances. On the other hand, the substances which we have shown to be composite are ferrous sulphide, rust, mercuric oxide, silver nitrate, and common salt. It will be seen that by combination of a *limited* number of elements, two, three, or four together, in varying proportions, all the known distinct substances might easily be accounted for. The list of elements whose individuality has been established appears upon the inside of the cover, at the end of this book; of these the larger number are not frequently encountered. More than 99 per cent of terrestrial material is made up of eighteen or twenty elements, of which the quantities of the first eleven, as estimated by F. W. Clarke, are given in the following table:

Oxygen	49.98	Calcium	3.51	Hydrogen	0.94
Silicon	25.30	Magnesium	2.50	Titanium	0.30
Aluminium	7.26	Sodium	2.28	Carbon	0.21
Iron	5.08	Potassium	2.23		99.61

The evidence of the spectroscope shows that the sun and stars contain many of the very same elements as does the earth.

Some of the Fundamental Ideas used by Chemists and the Corresponding Terms. — To the chemist it is above all important that he should be able to set forth in unambiguous terms the phenomena he observes and the inferences he draws. To do this he requires some fundamental ideas described by suitable words. Many of these ideas and terms we have been employing in order to accustom the reader to their use. It is now advisable to take them up more systematically.

Any particular specimen of matter, such as a piece of sulphur, a portion of water, a piece of ferrous sulphide, a fragment of granite, or some nitrate of silver solution, we call a **body**. There are thus as many bodies as there are discrete portions of matter. A body may be **heterogeneous**, or made up of visibly unlike parts, as granite and a **mixture** of iron powder and sulphur are; or it may be **homogeneous**, or alike in all parts, as are pieces of sulphur and ferrous sulphide and portions of water and silver nitrate solution.

Examination of these homogeneous bodies shows that the sulphur, ferrous sulphide, and water differ from the nitrate of silver solution in having but one **physical component**, while the last contains two components, nitrate of silver and water, separable by physical means. The last is like a mixture, only it is homogeneous. Again, the sulphur, ferrous sulphide, and water differ amongst themselves, the first being a simple body, with one **chemical constituent**, and the two others being compounds having each two chemical constituents. We speak of the *components* of a mixture or a solution because the parts are *laid together* and retain in the former case all, and in the latter much, of their identity. But of the materials in a chemical compound we use the word *constituents* because the parts are *built into each other* and have lost their identity. This distinction is very important. Unless it is understood, we cannot ourselves clearly describe a given body, or understand the description when given by someone else. When we state the result of our study of a body, as, for example, some liquid or solid in a test tube, we *always* give, *first*, the *physical components*. Thus we might say the material was composed of common *salt* in solution in *water*, or of a mixture of sand and sugar. Usually this is all the information that is needed, since the nature of the components named is presumably known. If, however, more information is demanded, then we proceed, next, to name the chemical constituents of each of the components. Thus, we might add that sodium and chlorine are the constituents of the salt. But we never reverse the order and give the constituents first, for, if we did, a chemist would understand us to mean that metallic sodium and yellow, gaseous chlorine were present in the tube, which would not be the case.

When a body, say a specimen of sulphur, contains *a little* of some other physical component, we speak of it as **impure** sulphur. This does not mean that it contains dirt in the ordinary sense of the term.

A little magnesium chloride is a common impurity in table salt (sodium chloride), and, by absorbing moisture, renders it more moist in damp weather than it would otherwise become. Absolutely pure bodies are unknown. "**Chemically pure**" means that the quantities of the impurities which the material is most apt to contain have been reduced below the amount which would interfere with the most exact chemical work for which the substance is commonly employed.

By convention we continually speak of "*pure*" hydrochloric acid, or of "*pure*" sulphuric acid, although there may be 60 per cent of water present in the former, and 7 per cent in the latter. By this we mean to distinguish the former from "commercial" hydrochloric acid, for example, which contains, in addition to the water, impurities like sulphuric acid and a coloring matter. The water is in fact disregarded, since it is assumed to be present in all cases.

In addition to the foregoing, there are three other sets of ideas, described by special terms, which are continually used in chemistry.

We distinguish one body, say one piece of sulphur, from another by its weight, form, or volume. Each particular specimen differs from every other in these **attributes**. These are general attributes possessed by matter and are used in chemistry for measuring quantity.

When all the bodies to which we should apply the name "sulphur" are compared, we find that, although some are in fine powder, and others in lumps of various shapes or in crystals, and thus differ in weight, form, and volume, they nevertheless have many qualities in common. These qualities we call **specific properties**, or properties common to a species. The material composing all the bodies of one species we call a **substance**. Some of the specific properties characterizing a substance and common to all specimens of one species are color, odor, crystalline structure, hardness, melting-point (temperature of fusion), solubility in water or other solvents, boiling-point (temperature above which, at 760 mm. pressure, the substance is gaseous), specific gravity, specific heat, and conductivity for electricity. Thus, sulphur is yellow, has little odor, crystallizes in the rhombic system, has a hardness of 2.5 on a scale of ten, has the m.-p. 114.5° C., is not perceptibly soluble in water but dissolves in carbon disulphide (41 parts in 100 at 18°), has the b.-p. 445° C., the sp. gr. 2, the sp. ht. 0.18, and is a very poor conductor. In the first two chapters, while presenting the experimental facts required for our

discussion, we have had to speak of *substances* very frequently (*e.g.* pp. 2, 3, and 5–8),* and have done so always in the above sense.

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain temperature, pressure, motion, or electric charge. These are impressed upon the body and do not inhere in it. We speak of them as **conditions of** the body rather than properties. In the use of the body they may be altered, and some of them may be removed or added, arbitrarily.

Thus there are three kinds of qualities to be considered. The *attributes*, like weight, form, and volume, do not belong to substances but do belong to bodies. The *specific properties*, like color, solubility, and odor, belong by right to substances. The *conditions*, like temperature and motion, belong to neither, for they can be altered without changing either the body or the substance.

Methods of Work and Observation in Chemistry.— It is not the end of chemical work to make generalizations or laws, like the characteristics of chemical phenomena (pp. 3, 11, 12, 18), or conceptions, like those dealt with in the preceding paragraph. These are simply the *means* by the help of which chemical work, whether it be investigation, commercial analysis, or manufacturing, may be carried on more systematically. Together they constitute our system for classifying the facts with a view to ready reference. The sample experiments (pp. 5–9), if reëxamined, will show that we there employed most of the categories of our classification which have so far been described.

Thus, in the experiment with iron and sulphur (p. 6), it was first our object to find out whether the bodies had interacted chemically on being mixed. To do this we noted the *specific properties* (p. 23)* of the substances separately. Using these properties we were able to **identify** the same substances in the mixture, and in

* References to previous pages are used in order to save needless repetition in writing. But the beginner requires endless repetition in his reading and must *form the habit* of examining, in conjunction with the current text, the parts referred to. The passages cited are, by the reference, *made part of the current text*, which will usually not be clear without them. The same remark applies to topics referred to by name. Such topics, if treated in later pages, are distinguished by the letters *q.v.*, and must be sought in the index.

All terms, and especially those borrowed from physics, if not perfectly familiar, must be looked up in a work on physics or in a dictionary.

this we found no substance with new properties. Part dissolved in carbon disulphide and reappeared after evaporation of the solvent as yellow, rhombic crystals, and the rest was all magnetic. In this connection we purposely omitted all mention of the quantity and temperature, because attributes (p. 23) like the former and conditions (p. 24) like the latter do not characterize substances (since they vary with each specimen), and cannot be used for identification. While all the specific properties, of which a few are mentioned on p. 23, find application in identification, the first eight on the list are those most frequently used. Coincidence in two or three specific properties is generally sufficient to establish identity.

Most of the properties cannot be recognized readily in *mixtures*, as a moment's thought will show. The general color and the specific gravity of a mixture, containing unknown substances in unknown proportions, for example, tell us little about the corresponding properties of the components. Now, there are few pure substances in nature or in the products of experiment, and many mixtures. Hence, **separation** of the components of a mixture usually of necessity precedes the process of identification just referred to. Thus, we first removed the sulphur by dissolving it and then recovered it by evaporation of the solvent, the *boiling-point* of the carbon disulphide (46°) being much lower than that of the sulphur (445°) and its vapor pressure, by virtue of which it evaporated at the temperature of the room, being therefore relatively high. We secured the iron because of its *insolubility*. Those specific properties which can be used for separating mixtures, as well as for identification, are therefore the most important of all. They are the melting-point (see Sulphur manufacture), solubility, boiling-point, specific gravity (see Gold extraction), and magnetic qualities, the last being applicable almost exclusively to iron, however.

In connection with this investigation we employed several of the common methods of **manipulation** used by the chemist. These methods are derived from the conceptions described in the last paragraph. Thus we **treated the mixture with a solvent** (Fig. 2), on the assumption that if it was heterogeneous (p. 22) the components would each behave as if alone present. We then **filtered**, a method invented for dealing with a heterogeneous mixture consisting of a solid and a liquid. **Decantation** is often used in such cases when the solid is specifically much heavier than the solvent and settles readily.

We allowed the carbon disulphide to **evaporate** spontaneously, and this is our favorite method of dealing with a mixture which is homogeneous, and therefore would run through a filter as a whole without suffering separation. When the liquid has a higher boiling-point than 50–60° C., as water has, we use heat from a steam-bath or Bunsen flame to promote the evaporation. In evaporation we allow the vapor of the liquid to escape, because it is the less volatile, dissolved body that we wish to examine. When we desire, on the contrary, to examine the liquid, the vapor must be condensed. This method, which we have not yet had occasion formally (see Exercise 2) to employ, is called **distillation** (Fig. 14). The jacket round the

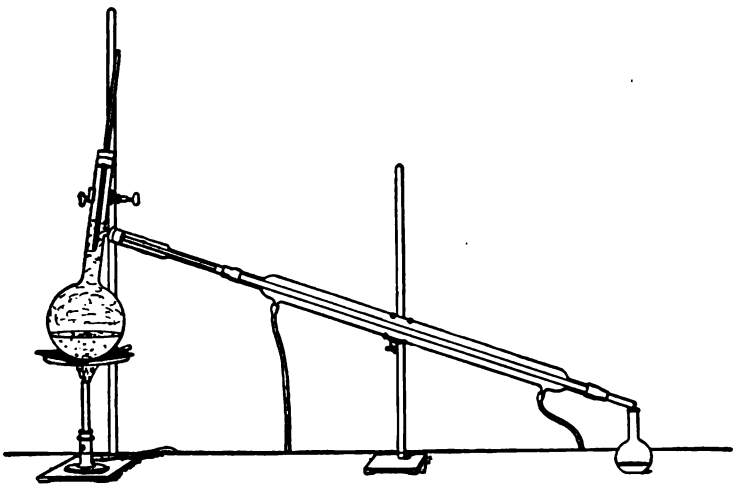

FIG. 14

long tube is filled with a stream of cold water, which, on account of its high specific heat, quickly cools and condenses the vapor. The resulting liquid is caught in a flask.

These methods may be adapted to the investigation of any similar problem. Thus, gunpowder is made by the intimate mixing of sulphur, charcoal, and saltpeter (potassium nitrate). If no chemical interaction whatever has occurred, a sample will be wholly separable into these components. If a partial change has taken place, a certain amount of material with different properties will be discovered in the mixture. If the change has been complete, no portion of the

original substances will be found. We must first study the specific properties of each of the ingredients separately, in order that a plan of separation may be devised, and that we may have a basis for comparison with the products of the separation.

It should be noted that our methods of investigating the products of nature and of the laboratory are purposely limited so as not to separate chemically combined, but only physically mixed forms of matter. After a physical individual has been isolated, and even then only if it has new properties, and is not recognized as a known substance, we next proceed to separate it into its chemical constituents so as to learn which constituents it contains and in what relative proportions by weight.

The experiments with mercuric oxide (p. 7)* and with silver nitrate (p. 8) simply rang the changes on the same conceptions, and repeated the same manipulations. In every case the specific properties — color, crystalline form, volatility, solubility, and so forth — by which separation and recognition were effected will be found to have been mentioned.

Summary. — In this chapter we have added considerably to our conception of the scope of chemistry (*cf.* p. 11). Although our survey is by no means yet complete, we may condense our results as follows:

Chemistry deals with the changes in composition and constitution which substances undergo and with the transformations of energy which accompany them. To convert the isolated facts into a science we classify related parts under laws, such as those of conservation of mass (p. 12) and of energy (p. 17), and under conceptions, such as those of internal energy (p. 17), element (p. 20), body (p. 22), substance (pp. 2–3, 21 and 23). We also distinguish between attributes, specific properties, and conditions (pp. 23–24). In the last paragraphs we have indicated briefly the use to which these conceptions and this classification are put.

The system of classification as a whole is part of the everyday mode of thought of the chemist, for thought consists largely in comparing and contrasting, and our system of classification furnishes the plan of this so far as chemistry is concerned. Learning chemistry consists, therefore, in large part, in learning this classification and becoming habituated to its use.

* See footnote to p. 24.

*Exercises.** — 1. What are the two most direct ways of showing a substance to be a compound? Illustrate each.

2. Discuss in detail the experiments with mercuric oxide (p. 7), and with silver nitrate (p. 8), showing what specific properties were used for separating and identifying the products, and how they answered the purpose. Which methods of manipulation were employed in the second experiment, and which method was used, essentially, in the first?

3. Define the following terms, and find illustrations of each, other than those given on p. 22: mixture, physical component, chemical constituent.

4. Describe, (*a*) a red-hot rod of iron, (*b*) an aqueous solution of sugar, employing all the terms given on pp. 22–24, so far as they are applicable.

5. What (*a*) elements and (*b*) substances are contained in an aqueous solution of sodium nitrate? Would it be correct to say that the simple substance oxygen is contained in it? What then is the difference in meaning between the terms "element oxygen" and the "simple substance oxygen"?

* The exercises should in all cases be studied with minute care. They not only serve as tests to show that the chapter has been understood, but very frequently (as in No. 1) also call attention to ideas which might not be acquired from the text alone, or (as in No. 5) assist in elucidating ideas given in the text which, without the exercises, might not be fully grasped.

CHAPTER III

INTRODUCTORY III

The Law of Definite Proportions, Fifth Characteristic of Chemical Phenomena. — The ways of forming or decomposing a compound, or of carrying out a more complex chemical change, may be varied indefinitely. The apparatus, the mode of experiment, and the proportions of the materials, may be altered at our will. But, in spite of an enormous amount of careful work, no case of variation in the proportion of the constituents *actually used* or *produced* in a given chemical action has come to light. If too much of one constituent, for example, is taken, a part simply remains unchanged. **In every sample of each compound substance formed or decomposed, the proportion by weight of the constituents is always the same.** This statement of fact is known as the **law of definite proportions.** Another form of statement, which is applicable more directly to complex chemical actions, is: The ratio by weight of any one of the factors or products of a chemical change to any other is constant.

The Measurement of Combining Proportions. — The most *exact* measurement of the proportions in which the elements combine to form compounds involves manipulations too elaborate to be gone into here. One or two brief statements, diagrammatic rather than accurate, will show the principles, however.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an **excess** of sulphur), we get free sulphur along with the ferrous sulphide (pp. 6–7), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of ferrous sulphide and iron gives the amount of sulphur combined with the known quantity of the latter.

As an example of the study of rusting, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass

oxygen over the heated metal (Fig. 15). If we limit the oxygen, part of the copper may remain unaltered; if we use it freely, the excess will pass on unchanged. The original weight of the copper, and the

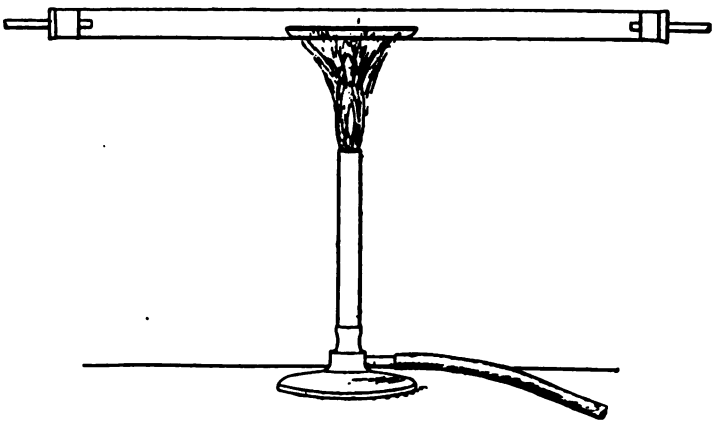

FIG. 15

increase in weight, representing oxygen, give us the data for determining the composition of cupric oxide. The data furnished by one rough lecture-experiment, for example, were as follows:

Weight of boat empty	3.428 g.
Weight of boat + copper	4.278 g.
Difference = **weight of copper**	**0.850 g.**
Weight after addition of oxygen	4.488 g.
Weight without oxygen	4.278 g.
Difference = **weight of oxygen**	**0.210 g.**

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

The results of quantitative experiments are usually recorded in the form of parts in one hundred. To find the percentage of each constituent, we observe that the proportion of copper is 85 : 85 + 21, or $\frac{85}{106}$ of the whole. That of the oxygen is $\frac{21}{106}$ of the whole. Thus the percentages are:

Copper,	$106 : 85 :: 100 : x$	$x = 80.2$
Oxygen,	$106 : 21 :: 100 : x'$	$x' = 19.8$

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportion. The percentages at present accepted as most accurate are 79.9 and 20.1.

In the case of mercuric oxide, we may decompose a known weight of the oxide (p. 7) and afterwards weigh the mercury and ascertain the oxygen by difference.

The following figures show some results of experiments like these, only two places of decimals being given. The numbers in parenthesis will be explained presently:

(1)	Cupric oxide			(2)	Mercuric oxide		
	Copper	79.9	$\left[\frac{31.8}{8}\right]$		Mercury	92.59	$\left[\frac{100}{8}\right]$
	Oxygen	20.1			Oxygen	7.41	
(3)	Water			(4)	Chlorine monoxide		
	Hydrogen	11.18	$\left[\frac{1.008}{8}\right]$		Chlorine	81.59	$\left[\frac{35.45}{8}\right]$
	Oxygen	88.81			Oxygen	18.41	

Combining and Equivalent Weights.— The percentages in the above list represent the true proportions by weight in the various compounds, but naturally the individual numbers constituting those proportions have no chemical significance whatever. They are arbitrary values selected so that the constituents of the proportion may together make 100. Each pair represents the constant ratio which is the mean result of numerous experiments.

We begin the effort to reduce these numbers to order by selecting one element as our starting-point, and by taking some convenient weight of it as the basis. As we shall see, it makes *no difference* what choice we make in either respect. To avoid waste of time, we shall, therefore, use oxygen, as it is the element generally preferred by chemists for the purpose. The reason for this preference will be apparent later (see pp. 35 and 37).

We should naturally be inclined to use 1 part of the element as our basis. But our later steps involve finding out what amounts of the other elements combine with this quantity, and we perceive that the amount in the case of hydrogen will be only 0.126 parts. We calculate this from (3): $88.81 : 11.18 : 1 : x$ ($= 0.126$). If, however, we take 8 parts of oxygen, this amount of hydrogen is also increased eight times and becomes 1.008. As no element is found to combine in smaller proportions than hydrogen, we are satisfied that a scale

for our numbers based on 8 parts of oxygen will not involve any values less than 1. The choice of scale is purely one of convenience.

We now proceed to calculate from the data given above the weight of each of the other four elements which combines with 8 parts of oxygen. From (1) we calculate this weight of copper, thus, 20.1 : 79.9 : : 8 : x (= 31.8 parts of copper). Similarly we find that 8 parts of oxygen combine, in (2) with 100 parts of mercury, in (3) with 1.008 parts of hydrogen, and in (4) with 35.45 parts of chlorine. Oxygen unites with almost all the known elements, and these four compounds have been chosen simply as a sample group.

Oxygen	Copper	Mercury	Hydrogen	Chlorine
8	31.8	100	1.008	35.45

Now chlorine combines, not only with oxygen, but also with copper, mercury, and hydrogen, and measurement shows that the combining proportions are represented, *exactly, by the very same numbers as before.* From the two independent facts that 8 parts of oxygen combine with 31.8 parts of copper and with 35.45 parts of chlorine, we could not possibly have foretold the proportions in which copper and chlorine would combine with one another. Yet measurement shows it to be 31.8 : 35.45 precisely. In the following table the proportions of the elements are placed under the corresponding parts of the names of the compounds with chlorine:

Cupric Chloride	Mercuric Chloride	Hydrogen Chloride
31.8 : 35.45	100 : 35.45	1.008 : 35.45

That weight of each element which combines with 8 parts of oxygen (or 1.008 parts of hydrogen) is known as **the equivalent weight** of the element. These weights are equivalent because they hold identical amounts of oxygen (or hydrogen) in combination.

If additional elements had been included in the group, a combining number could have been found for each, and seeming coincidences of the same nature would have multiplied rapidly. Thus, sulphur unites with hydrogen to give hydrogen sulphide. If, to maintain the same scale, we use 1.008 parts of hydrogen in expressing the proportion, we find that the combining ratio is 1.008 : 16.03. This result could not enable us to predict the proportion of copper to sulphur in

cupric sulphide, but measurement shows it to be 31.8 : 16.03. And mercury and sulphur unite in the proportion 100 : 16.03.

SULPHUR, with the value 16.03, may therefore be added to the series of equivalent weights.

Law of Multiple Proportions. — One other remarkable fact remains to be noted. There are *two different* compounds of copper with oxygen. Cuprous oxide (*q.v.*), the one not mentioned hitherto, is found in nature as a dark-red mineral which is entirely different from cupric oxide in physical properties. It can also be prepared in the laboratory, but not by simply passing oxygen over heated copper. Now, analysis shows that in cuprous oxide the proportion of copper combined with 8 parts of oxygen is 63.6. This new number for copper is not unrelated to the corresponding value in cupric oxide (*viz.* 31.8), for it is exactly twice as great. Again mercury forms mercurous oxide (see p. 34) as well as mercuric oxide and in the former the proportion of oxygen to mercury is 8 : 200. The proportions of mercury uniting with 8 parts of oxygen are therefore 100 and 200, and no other proportions are known. Still again, 1.008 parts of hydrogen unite with 8 parts of oxygen in water and with 2×8 parts of oxygen in hydrogen peroxide. The fact suggested by these three examples is a general one. It was discovered by Dalton (1804) and was embodied by him in a statement known as the **law of multiple proportions**, which ran somewhat as follows: **If two elements unite in more than one proportion forming two or more compounds, the quantities of one of the elements, which in the different compounds are united with identical amounts of the other, stand to one another in the ratio of integral numbers, which are usually small.**

The Law of Combining Weights, Sixth Characteristic. — The reader should now examine carefully the following table of combining proportions. It includes *all* the compounds made up of pairs of the six sample elements under consideration, so far as the existence and composition of such compounds have been determined with certainty. The substances in black type are the ones from whose composition we originally derived the combining numbers, the others illustrate the uniform recurrence of the same numbers:

Cupric oxide	**Mercuric oxide**	**Hydrogen monoxide (water)**
31.5 : 8.00	100.0 : 8.00	1.008 : 8.00
Cuprous oxide	Mercurous oxide	Hydrogen peroxide
2 / 31.5 : 8.00	2 / 100.0 : 8.00	1.008 : 2 × 8.00
Cupric sulphide	Mercuric sulphide	**Hydrogen sulphide**
31.5 : 16.03	100.0 : 16.03	1.008 : 16.03
Cuprous sulphide	Mercurous sulphide	
2 / 31.5 : 16.03	2 / 100.0 : 16.03	
Cupric chloride	Mercuric chloride	Hydrogen chloride
31.5 : 35.45	100.0 : 35.45	1.008 : 35.45
Cuprous chloride	Mercurous chloride	
2 / 31.5 : 35.45	2 / 100.0 : 35.45	
Sulphur dioxide	**Chlorine monoxide***	Sulphur monochloride
16.03 : 2 / 8.00	35.45 : 8.00	2 × 16.03 : 35.45
Sulphur trioxide	Chlorine dioxide	Sulphur tetrachloride
16.03 : 3 / 8.00	35.45 : 4 × 8.00	16.03 : 2 × 35.45

It will be observed that the same number serves always to express the combining proportions of a given element, provided that multiplication by an integer is permitted when necessary. There are also some combinations of three of the same elements in one compound. But even in such cases the fundamental numbers still reappear. Thus oxygen, chlorine, and hydrogen combine in the proportions: 2 / 8 : 35.45 : 1.008, 6 / 8 : 35.45 : 1.008, and 8 × 8 : 35.45 : 1.008. Nor is the recurrence of a fundamental number an exclusive property of the six elements we have chosen for illustration. A vast table containing every known element, and every compound of every element, if prepared in the same way as that given above (by starting with a fixed number for one element and calculating the combining proportions in all the compounds with this number as a basis), would show that every element used an individual, fundamental number, or integral multiples of this number, in every one of its combinations. No exceptions to this rule would be found in the whole mass of data.

The law of combining weights may be put briefly thus: **The proportions by weight in which all chemical combinations take place can be expressed in terms of small integral multiples of fixed numbers, called combining weights, one for each element.** It describes what is perhaps the most striking of all the characteristics of chemical action.

If the reader will now reëxamine carefully the way in which the

data were handled, the following significant facts will be noted: (1) Oxygen was made the starting-point of the system and the value 8 was assigned to its combining weight.* Had a different value been used, all the numbers would have been different. But the change would have affected all the numbers in the same proportion and so only the *scale* of the numbers would have been affected. An individual combining number, one for each element, would have still recurred wherever the element itself appeared. (2) Even use of another element as the initial one would not have prevented the discovery of the law. Thus with hydrogen as the initial element, and the value 1.008, no change whatever would have been noted. With a different value for hydrogen, a change of scale in all the numbers would have followed, but individual combining weights would have appeared as before. (3) Finally, if cuprous oxide had been used instead of cupric oxide for the first proportion, the value found for copper would have changed to 63.6, while the other numbers would have remained unaffected. But this number would serve as the combining weight of copper just as well as 31.8, for the composition of cupric oxide can be expressed by the proportion $63.6 : 2 \times 8$ as well as by $31.8 : 8$, and that of cupric sulphide by $63.6 : 2 \times 16.03$ as well as by $31.8 : 16.03$. An important conclusion therefore follows from these considerations, and we shall have occasion to use it presently, namely, that any one or more of the equivalent weights (with scale oxygen = 8) may be separately multiplied by an integer without its usefulness as a member of the series being at all impaired.

The importance of the fact described in the law of combining weights cannot be emphasized too strongly. Without this fact, the remembering of the compositions of chemical substances, necessary as it is to the chemist, would have been completely beyond the power of any ordinary memory. With it, the task becomes comparatively

* Oxygen was chosen as the basis of the system because the exact determinations of the combining weights of most of the elements have actually been made by direct union with oxygen or with the help of but one intermediate step. If the question had been one of mathematics, hydrogen, the element with the lowest combining proportions, would have furnished the basis and unit of the scale. But the question was the practical one of getting the most accurate measurements for the relative magnitudes of the numbers, so oxygen was chosen instead. Nevertheless, the value 8 was selected in order that the advantage of having a mathematical unit, or something close to it, in the combining weight of hydrogen, might be retained also.

simple. It is only necessary to decide on the best system of values for the combining weights, and then, *regarding the value of this for each element as the unit of weight for that element*, to express the proportions of the element in every compound by the proper multiples. Thus, given a list of the combining weights, one for each element, only the small integral multiples have to be kept in mind in connection with each compound.

The reader will require a little time, however, before he becomes accustomed to the use, not of a single unit of weight, but of a different one for each element. Chemistry is the only science in which the physical unit of weight, which is the same for all materials, is not employed for every purpose. The physical manipulations of the chemist are carried out with the use of physical units, but the chemical results are expressed in terms of individual unit quantities of the several elements, the combining weights.

The individual units actually used for each element are not in all cases identical with those we have given. The final values will be discussed in the next section.

Atomic Weights. — The chemist frequently uses the idea of equivalents and the values we have given them. But far more often he employs a slightly differing set of numbers, which, for reasons that will appear in a subsequent chapter, he calls **atomic weights.** The following list shows the elements whose equivalents we have been discussing, along with one or two others, added by way of furnishing a fair sample, and gives both sets of weights for the purpose of comparison:

Element.	Equivalents (Combining Weights).	Atomic Weights.	Element.	Equivalents (Combining Weights).	Atomic Weights.
Oxygen	8	16	Iron	27.95	55.9
Copper	31.8	63.6	Magnesium . .	12.18	24.36
Sulphur . . .	16.03	32.06	Carbon	3.00	12.00
Mercury. . . .	100.0	200.0	Aluminium . .	9.03	27.1
Chlorine . . .	35.45	35.45	Sodium	23.05	23.05
Hydrogen . . .	1.008	1.008	Bromine . . .	79.96	79.96

It will be seen that some equivalents have been multiplied by two, the first four and those of iron and magnesium, for example; some

have been multiplied by three, like that of aluminium; some by four, like that of carbon; and some remain unchanged, like those of chlorine, hydrogen, sodium, and bromine.

The reasons for this manipulation of the simple equivalents found by experiment are based upon theoretical considerations. As it is impossible, until we reach certain important facts which cannot be introduced here, to explain these considerations, the discussion of the reasons for the changing of the numbers will be postponed until after these facts are before us. Suffice it to say that great advantages are found to attach to these modifications in the values. The step from equivalents to atomic weights (*q.v.*) is taken before the justification of it can be given, because otherwise formulæ (see next chapter) could not be used in the earlier chapters, and so the advantages their employment offers would be sacrificed.

The atomic weight is the unit of weight (p. 36) actually used in expressing the proportions of each element in all its compounds. The integral factors are, of course, different from those which would be employed in expressing the composition of the same substance in terms of equivalents, because many of the latter have been multiplied by small integers already in course of being made into atomic weights. But the multiplication has in every case been by an integer, so that the new numbers are just as serviceable as the old (p. 35).

To the reasons given above for the choice of oxygen as the fundamental element, and the value 8 for its combining or equivalent weight, one other may now be added. The majority of the atomic weights, calculated on this basis from the experimental results, fall so close to being integers that the nearest round numbers are exact enough for ordinary use. Thus in the above list nine of the twelve atomic weights are within 0.1 of the nearest whole number. This convenience disappears when, for example, hydrogen with the value 1 is made the basis.

The reader will inevitably find difficulty at first in thoroughly grasping the significance of these numbers. It may, therefore, be of some assistance if a hint is thrown out which will suggest a concrete basis for this curious property. These numbers appear to mean that, when we wish to make a chemical compound, we may choose any two elements from the list, and, if it is found that they can combine at all, we have only to take the atomic weights, worked out from other combinations of each element, and we shall find that they

will exactly suffice for this case of chemical union. If *complete* combination of both materials does not take place, then trial will quickly show what multiples of the atomic weights will result in this. The situation seems to suggest that the constructing of chemical compounds depends upon the putting together of ready-made "parts," like those of a watch or a bicycle. The parts seem to be "interchangeable," and each element seems to be furnished to us by nature in ready-made packets suitable for application in building up any chemical structure.

A complete list of atomic weights is printed on the inside of the cover at the back of this book.

Summary. — This chapter adds an important item to our statement of the scope of the science (*cf.* p. 27), which, therefore, now reads as follows: Chemistry deals with the *quantitative* study of the changes in composition and constitution which substances undergo and with the transformations of energy which accompany them. To express the quantitative relations which are observed, a different unit of weight is employed for each element, and is known as the atomic weight of the element.

Exercises. — 1. To test the correctness of the statements on p. 35, take mercury as the basal element and 250 as its combining weight, and work out from the data on pp. 31 and 32 (second line from the foot) the corresponding combining weights of the other five elements. Then show that the values obtained have the same property as have the equivalents.

2. Express in terms of atomic weights, or their integral multiples, the composition of cupric oxide, cupric chloride, sulphur monochloride.

3. Show that doubling the atomic weight of chlorine would give an available combining number.

CHAPTER IV

INTRODUCTORY IV

A CONSIDERATION of the contents of the foregoing chapter will show that the complete description of a chemical change must be exceedingly involved. In a moderately complex action, such as that of sodium chloride upon silver nitrate, we should say that sodium chloride, composed of one atomic weight each of sodium and chlorine, when brought in contact with silver nitrate, composed of one atomic weight each of silver and nitrogen and three atomic weights of oxygen, *gave* silver chloride, composed of one atomic weight each of silver and chlorine, and sodium nitrate, composed of one atomic weight each of sodium and nitrogen and three atomic weights of oxygen. Such a statement, while it would give all the facts in the quantitative point of view, would be difficult to grasp and lacking in perspicuity.

Symbols, Formulæ, and Equations. — In order to represent the nature of a chemical change in a form which may be taken in at a glance, the chemist is in the habit of using certain **symbols**, first introduced by Berzelius. Thus, the letters Ag represent one atomic weight (*i.e.*, 107.93 parts) of silver (*argentum*), and O represents one atomic weight (*i.e.*, 16 parts) of oxygen. In other words, the symbol of an element means one chemical unit weight of the element. Since many elements begin with the same initial, two letters have frequently to be used to distinguish them. When the names of the elements are not the same in all languages, resort is frequently had to Latin. Thus, Cu stands for one combining weight of copper (*cuprum*), Fe is used for iron (*ferrum*), Hg for mercury (*hydrargyrum*). From German we have Na for sodium (*natrium*) and K for potassium (*kalium*). To represent a compound, the symbols of the elements which it contains are placed side by side, small numbers indicating multiples of the atomic weights where they occur. Thus, sodium chloride is represented by the expression NaCl, silver nitrate by the symbols $AgNO_3$. A combination of symbols is called a **formula**.

The symbols composing a formula, taken by themselves, do not stand for any definite quantity; each is one factor of a proportion. Ag means the proportion of 107.93 parts of silver to the proportions of the other elements represented by the other symbols which may be connected with it.

The value of these symbols lies, not only in the compact way in which the resulting formulæ present the composition of compounds, but also in the use which may be made of them in showing at a glance the details of a chemical change. The chemical action just mentioned appears as follows:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3.$$

This expression contains all that was conveyed by the words which were written out in full above. The arrow indicates that the materials on the left-hand side pass, in the chemical transformation, into those on the right-hand side. Such symbolic expressions are called **equations.**

One other variation is in frequent use. The equation for the formation of rust, if we left the water which enters into its composition out of the question, would run thus:

$$2Fe + 3O \rightarrow Fe_2O_3.$$

It will be observed that we employ the form 2Fe before combination and Fe_2 (in Fe_2O_3) after it. The reasons for this usage will become clear as we proceed. We note simply that 2Fe means 2 separate atomic weights of iron, as $3Fe_2O_3$ would mean three separate **formula-weights** of oxide of iron. The same *substance* (*cf.* p. 21), iron, might appear as 5Fe or 8Fe in other equations, according to the proportion needed. But Fe_2O_3 is a group of five atomic weights united chemically. The *substance* ferric oxide never contains anything but two atomic weights of the *element* iron, and its formula is invariable. Thus the *regular* integers multiplying the atomic weights in the composition of a particular compound are written *after* the symbols of the elements, while more arbitrary coefficients which change from one use of the substance to another are written in front. When no coefficient appears in front of a symbol or formula, 1 is to be understood.

Making Formulæ. — To make the formula of a compound substance, assuming the formula to be unknown, two kinds of informa-

tion are required. We ascertain (1) by measurement the proportion by weight of the constituents in the compound. We require also (2) to know the chemical unit weights — the atomic weights — which have been accepted by chemists for each constituent element. By factoring the terms of the first proportion so that one factor in each case is the atomic weight, we discover whether multiples of the atomic weights will be required to represent the composition of the substance, and if so what these must be. An illustration will make the process clear.

Suppose the problem is to make the formula of dried rust. By weighing before and after the change, we get the weight of the iron and of the corresponding amount of oxygen in the rust it produces. If we took 2 g. of iron we should get about 2.86 g. of rust. So that the proportion of iron to oxygen is $\frac{2}{0.86}$. Now, in the formula, the same ratio must be represented by means of multiples of the atomic weights (p. 37). We therefore divide the quantity of each element by the corresponding atomic weight. This gives us the factors by which the atomic weights are to be multiplied. The atomic weights are 55.9 and 16 respectively: $2 \div 55.9 = 0.0358$, and $0.86 \div 16 = 0.0537$. The proportion $\frac{2}{0.86}$ then becomes $\frac{55.9 \times 0.0358}{16.0 \times 0.0537}$. Now this proportion must be capable of expression in terms of *integral* multiples of the atomic weights. We find that the greatest common measure of the two factors is 0.0179. Dividing above and below by this, we obtain the ratio $\frac{55.9 \times 2}{16.0 \times 3}$. Substituting the symbols for the atomic weights, the proportion appears as $\frac{Fe \times 2}{O \times 3}$, and the formula is therefore Fe_2O_3. It is obvious that setting the symbols down side by side is not sufficient. We must determine by measurement the factors by which they are to be multiplied.

Making Equations. — To make the equation representing a chemical change we note, (1) what substances were used, and ascertain, by study of their properties, what substances were formed. Then we learn (2) the formulæ of the substances used and pro-

duced. This we do either by measurement and calculation, as shown above, or we find in the text the formulæ as they have been determined by the experimental work of chemists. From these we prepare (3) a skeleton equation which, in the instance discussed, would appear thus:

$$Fe + O \rightarrow Fe_2O_3.$$

We are careful to place the initial substances on the left, and to point the arrow towards those which are produced. Finally (4) we "balance the equation" by placing the proper coefficients before the formulæ. This last operation requires experience for its rapid performance. A good rule is to begin by picking out that one of the formulae which contains the largest number of atomic weights, no matter upon which side it appears. Here, this formula is Fe_2O_3. We then reason that, to obtain Fe_2 we require 2Fe, and to obtain O_3 we require 3O, and accordingly we place these coefficients before the appropriate symbols, thus:

$$2Fe + 3O \rightarrow Fe_2O_3.$$

It is hardly necessary to add that a chemical equation gives the proportions of the materials and nothing more. The physical conditions, for example, whether the substances are dissolved in a liquid, or are in the state of gas, or are at a high temperature, have no place in it. The physical properties of the substances concerned, and also the energy in the form of heat or electricity which may appear or disappear in the process, are likewise left entirely out. A question in regard to the nature of a particular chemical change demands in answer a full statement of all these things. The equation is therefore an essential part, but only a part, of such a statement.

Units of Measurement in Chemical Work. — In chemical work temperatures are invariably measured on the Centigrade scale. The temperature of a mixture of ice and water is the zero point. The temperature of the steam which rises from water boiling under a pressure of one atmosphere is represented by 100°. The interval between those two points is divided into one hundred equal parts.

For the expression of length, weight, and volume, the metric system is employed. The unit of this system is the meter, which is subdivided into decimeters, centimeters (cm.), and millimeters (mm.).

For small measurements the last subdivision is taken as the unit. A cubic centimeter (c.c.) is the unit of volume for small measurements. For larger ones the liter, which contains 1000 cubic centimeters, is used. The unit of weight is that of one cubic centimeter of water at 4°, the temperature of maximum density. This is called the gram.* For larger amounts of material the kilogram, which contains 1000 grams (1000 g.), is frequently employed. The meter is equal to about 39⅓ inches in ordinary measures, and the centimeter is very nearly ⅖ of an inch. One liter is about $\frac{1}{28}$ of a cubic foot and contains 61 cubic inches or 35 fluid ounces. One hundred grams is about 3½ ounces avoirdupois, and one ounce equals 28.35 grams.

Calculations in Chemistry. — In the laboratory it is frequently desirable that we should know what amount of some substance may be obtained by a given chemical action from another, or what amount of material must be used to obtain the desired amount of some product. This information is readily accessible, since measurements of quantity in connection with most chemical changes are on record. The simplest and most easily handled form of this record is found in the formulæ of compounds, and in the equations representing the changes which they undergo. It is most convenient, therefore, when a question of this kind occurs, *to ascertain and write down, first, the equation.* Having then before us the information in regard to the quantities in the most condensed form, we may use such parts of this information as are required for the problem in hand.

Suppose, for example, that the question is in regard to the weight of oxygen which may be obtained from 120 g. of mercuric oxide. We write down the equation, and, if the numbers are not familiar to us, we ascertain the atomic weights, a table of which is printed on the inside of the rear cover of this book. These we place then below the symbols by which they are represented, thus:

$$\underset{200+16}{HgO} \rightarrow \underset{200}{Hg} + \underset{16}{O}$$

Reading this equation, it appears that one formula-weight, or 216 parts by weight, of mercuric oxide give one atomic weight, 16 parts,

* In point of fact, the gram is the one-thousandth part of the weight of the standard kilogram kept in Paris. This differs from the weight of 1 c.c. of water at 4° by less than 0.01 per cent.

of oxygen, and the question is, What weight of oxygen will be obtained from 120 grams of the oxide? The answer may be stated by simple proportion: 216 : 16 : : 120 : x, or $16 \times \frac{120}{216} =$ Answer.

The reader must conquer a tendency to speak of the symbol O as representing "1 part" of oxygen: it stands for *16 parts.* The word "part" refers to physical units exclusively.

It will be noticed that not all the data which we have written down are necessarily used. In general, only two of the three or more weights which the equation represents will be required.

Exercises. — 1. What weight of mercury is obtained from 120 g. of mercuric oxide?

2. What weight of mercuric oxide will furnish 20 g. of oxygen?

3. What weight of rust may be obtained from 10 g. of oxygen?

4. What weight of silver chloride is obtained from 50 g. of silver nitrate (p. 40)?

5. How much silver is contained in 100 g. of an impure specimen of silver chloride which is 33 per cent sand?

6. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance?

7. What are the formulæ of the substances possessing the following percentage compositions? The percentages are to be divided by the atomic weights just as were the actual weights in the illustration on p. 41.

I		II		III	
Magnesium,	25.57	Sodium,	32.43	Potassium,	26.585
Chlorine,	74.43	Sulphur,	22.55	Chromium,	35.390
		Oxygen,	45.02	Oxygen,	38.025

8. What are the percentage compositions of substances possessing the following formulæ: Mn_3O_4, KBr, $FeSO_4$?

9. Compare the formula of mercurous oxide, found in 6, with that of mercuric oxide, and show how the compounds illustrate the law of multiple proportions (p. 33).

10. Using the proportions given on p. 34, calculate the formulæ of all the compounds in the table. Compare in each case the factors which multiply the symbols (and therefore the atomic weights) with those used in the table to multiply the equivalent weights. Explain the differences where they occur.

CHAPTER V

OXYGEN

Historical and Introductory. — Almost one-quarter of the atmosphere, by weight, is *free* oxygen. Water contains nearly 89 per cent of oxygen in combination, and this element constitutes about 50 per cent of common materials like sandstone, limestone, brick, and mortar. On account of its predominance over other elements in quantity (p. 21), and the exceptional capacity which it exhibits for forming compounds with a great variety of other elements, the systematic study of chemistry may conveniently be begun with oxygen.

While many elements which are less easily obtainable than oxygen have been recognized as distinct substances for many centuries, oxygen did not attain this position until it was prepared, first by Scheele in Sweden in 1771–3 and, independently, by Priestley in 1774. The latter was particularly interested in examining the nature of the gases which were evolved by some materials when heated. He found that mercuric oxide gave off an unusual amount of a gas, or " air " as he called it. Priestley discovered that this gas supported combustion extremely well and, later, that it was respirable and favorable to the life of small animals, such as mice. He did not, however, recognize that atmospheric air was a mixture, and that the substance he had obtained was in reality identical with that component of the air which has the same properties.

Meanwhile Lavoisier, in Paris, who had been studying the rusting of metals in the air, heard of Priestley's experiments, and demonstrated that the latter's " good air " was really a component of common air, and combined with metals when they formed rusts, or " calces," as they were then called. He proved this conclusively by heating mercury in an inclosed volume of air. The red mercuric oxide accumulated on the surface of the mercury and simultaneously the air suffered a shrinkage of about one-fifth of its volume. The residual gas, nitrogen, no longer supported combustion or life. The

oxide on being heated more strongly by itself gave off a gas whose volume exactly corresponded with the shrinkage undergone by the inclosed air, and this gas possessed in an exaggerated degree the properties which the air had lost. The proof that oxygen was a constituent of the atmosphere was therefore complete. Lavoisier, in the mistaken belief that the new element was an essential constituent of all sour substances, named it **oxygen**, or acid-producer (Gk. ὀξύς an acid, γεννᾶν to produce).

Preparation of Oxygen. — 1. Oxygen may be separated from the other substances mixed with it in the atmosphere by liquefying the air (see Liquid air), allowing the nitrogen, which is more volatile, to escape, and finally compressing into tanks the oxygen which evaporates last. This is a purely mechanical process.

2. There are many compounds which, when heated to temperatures under 2000° such as we can obtain with the aid of a Bunsen burner, a coal fire, or a blast-lamp, give up their oxygen. Some of them are minerals, but most of them are manufactured articles. Of the minerals, pyrolusite (manganese dioxide, MnO_2), employed by Scheele, is an example. It usually contains the elements of water also, and hence moisture is evolved at the same time. A substance identical with the mineral hausmannite (Mn_3O_4. For the equation see p. 50) remains. Amongst the artificial sources are mercuric oxide, expensive, but historically interesting (p. 7); barium peroxide, used in manufacturing oxygen on a large scale (Brin's process); and potassium chlorate, the most convenient for laboratory use.

Brin's Oxygen Process starts from barium oxide (*q.v.*). Barium oxide BaO closely resembles quicklime CaO, but differs from this substance in the fact that when heated in air to about 500°, it rapidly acquires additional oxygen and gives barium peroxide. When barium peroxide is raised to 1000°, this extra oxygen is given up again. Barium oxide contains one chemical unit weight each of the two constituents and takes up another of oxygen, so that the equation for the primary action is: $BaO + O \rightarrow BaO_2$. The subsequent decomposition of the peroxide, during the stage in which the oxygen is made, is the exact opposite: $BaO_2 \rightarrow BaO + O$.* The commer-

* In cases where an action is reversible, and the direction depends on conditions which may be altered, we write both equations in one:

$$BaO + O \rightleftarrows BaO_2.$$

cial advantage of the method lies in the fact that the barium oxide remaining after the second stage can be used over and over again. This, as will be seen, is in reality a chemical method of obtaining oxygen from the air.

In practice the barium oxide is maintained at a temperature of 700°, intermediate between the two just mentioned, and air is forced under pressure into the tubes containing the oxide. A valve at the extremity of the tubes permits the escape of the nitrogen. When the combination with oxygen is completed, the pumping apparatus is reversed, and, a partial vacuum being created, the oxygen in combination is given off without any alteration in temperature being necessary. Thus a great waste of fuel is avoided, and the process is rendered more nearly continuous. This method furnishes oxygen about 96 per cent pure, and suitable for sale in compressed form in iron cylinders.

Potassium Chlorate (*q.v.*) is a white crystalline substance used in large quantities in the manufacture of matches and fireworks. When heated in a tube similar to that in Fig. 5, it first melts (351°) and then, on being more strongly heated, it effervesces and gives off a very large volume of oxygen. Examination shows that the whole of the oxygen it contains can be driven out. The white material which remains after the heating is identical with the mineral sylvite. To the chemist it is known as potassium chloride, and, when decomposed, it yields potassium and chlorine in the exact ratio of their atomic weights. Its formula is thus KCl. We may infer, therefore, that the composition of the original substance will be representable by the formula $KClO_x$, where x is the number of atomic weights of oxygen. Measurement and calculation show $x = 3$. The formula is therefore $KClO_3$, and the equation for the decomposition (see, however, under Perchlorates):

$$KClO_3 \rightarrow KCl + 3O.$$

A peculiarity of this action is that admixture of manganese dioxide increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence, in its presence, and it is generally mixed with the chlorate in laboratory experiments (Fig. 16), a sufficient stream of the gas is obtained at a relatively low temperature (below 200° see p. 55).

Physical Properties of Oxygen. — Oxygen resembles air in being a colorless, tasteless, and odorless gas. Its density, using the physical standard of air = 1, is 1.105. If hydrogen is the standard, oxygen is 15.900 times (Morley) as heavy. One liter of oxygen, at 0° and 760 mm. barometric pressure, weighs 1.42900 grams (Morley). The gas dissolves to some extent in water, the solubility at 0° being

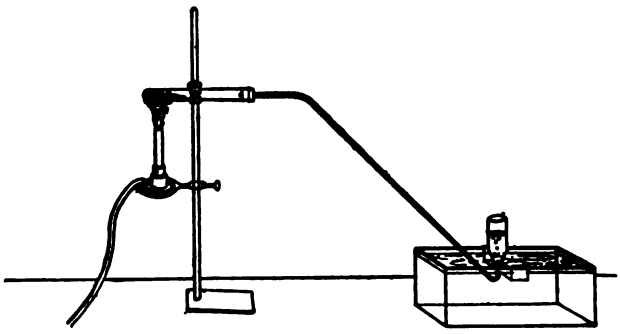

FIG. 16

four volumes of gas in one hundred volumes of water (at 20°, 3 : 100). Liquid oxygen, which was first made by Wroblewski, has a pale-blue color, and boils under one atmosphere at − 182.5°. Its specific gravity at − 182.5° is 1.13 (water = 1): that is to say, 1 c.c. weighs 1.13 g. By cooling with a jet of liquid hydrogen, Dewar froze the liquid to a snow-like, pale-bluish solid. A tube of liquid oxygen is very noticeably attracted by a magnet.

Chemical Properties of Oxygen. — Sulphur, when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 17), giving out much heat and producing a familiar gas having a pungent odor (sulphur dioxide). This odor is frequently spoken of as the " smell of sulphur," but in reality sulphur itself has no odor, and neither has oxygen. The odor is peculiar to the compound of the two. The mode of experimentation can be changed and the oxygen led into sulphur vapor through a tube. The former then appears to burn with a bright flame, giving the same product as before. For the formulæ and equations for this and the following actions, see next section.

Warm phosphorus combines with oxygen with even greater vigor, and forms a white, powdery, solid compound (phosphoric anhydride), which absorbs moisture from the aqueous vapor in the air and quickly forms a solution in this water. In both these cases the products differ from oxygen, not only in odor and in other physical properties, but notably in that, when shaken with water, they dissolve and interact to form acids (see below).

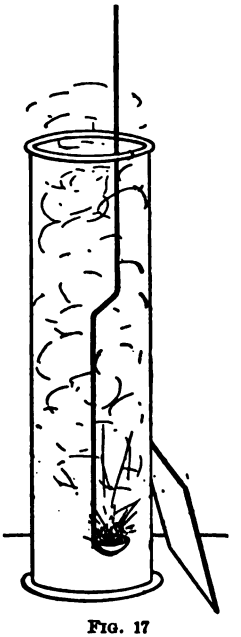

FIG. 17

Burning carbon, in the form of charcoal, glows much more brightly in oxygen than in ordinary air. The product is an odorless gas (carbon dioxide). When this gas is shaken with "lime-water," a solution of calcium hydroxide $Ca(OH)_2$ (*q.v.*, and see p. 71), a white precipitate of calcium carbonate $CaCO_3$ is formed.

Finally, metallic iron, which is simply rusted by air (diluted oxygen), burns in pure oxygen with surprising brilliancy. Globules of a molten product fall from the iron and, when they have cooled, are found to consist of a dark-gray brittle material, which we recognize as identical with blacksmith's hammer scale and with a well-known ore of iron (magnetic oxide of iron).

The results of a long series of experiments like the above enable us to summarize the **chemical properties of oxygen.** The gas unites directly with nearly all the simple substances, and often, though not always, with the same vigor as in the case of these examples. In the case of one or two elements, such as gold and platinum, the compounds are obtainable by double decomposition, and not directly. With the five members of the helium group, of which no chemical compounds are known, and with fluorine, oxygen does not combine.

Oxygen can unite with many of the same elements when they are already in combination. Wood, for example, is composed of carbon and hydrogen, with a certain amount of oxygen. When previously heated, it is decomposed, and the constituents unite with oxygen forming carbon dioxide and water.

The Making of Equations Again. — To learn the exact nature of interactions like those used as illustrations above, quantitative experiments must of course be made. Thus, for example, a known weight of sulphur is placed in a porcelain boat (Fig. 18), which has

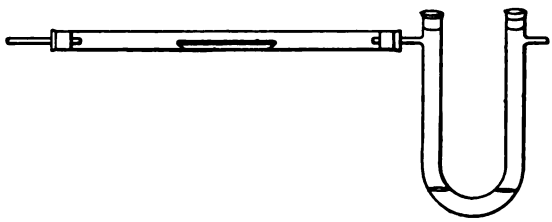

FIG. 18

already been weighed. The U-shaped tube to the right contains a solution of potassium hydroxide which is capable of absorbing the resulting gas. The oxygen enters from the left. When the sulphur is heated, it burns in the oxygen, and the loss in weight which the boat undergoes shows the amount of sulphur consumed. The gain in weight of the U-tube shows the weight of the compound produced. By subtracting, we get the quantity of oxygen. The proportion of the constituents and the steps in the calculation (p. 41) are as follows:

	PERCENTAGE		AT. WT.		FACTOR			+1.561
Sulphur,	50.05	=	32.06	×	1.561	=	S × 1.561	S × 1
Oxygen,	49.95	=	16.00	×	3.122	=	O × 3.122	O × 2

The formula of the product is therefore SO_2 and the equation $S + 2O \rightarrow SO_2$.

Similarly, phosphoric anhydride may be shown to have the formula P_2O_5, carbon dioxide CO_2, and magnetic oxide of iron Fe_3O_4. To make the equations representing their formation, the rules given on pp. 41–42 should be applied.

To make the equation for the formation of oxygen and hausmannite by heating manganese dioxide (p. 46) the same rules are used. The skeleton equation is: $MnO_2 \rightarrow Mn_3O_4 + O$. These being the formulæ of the substances actually concerned, in balancing the equation it is not permissible to alter them except by placing coefficients in front. The most complex formula is Mn_3O_4 and, to get a sufficient number of atomic weights to produce it, at least

$3MnO_2$ is required. This furnishes 3Mn and 6O, so that, after using 4O, there remains 2O:

$$3MnO_2 \rightarrow Mn_3O_4 + 2O.$$

Oxides. — Substances containing one element in combination with oxygen are called **oxides**, and processes like those described above are called oxidizing processes, or **oxidations**. When the same element forms more than one oxide, the names of the oxides indicate the differing proportions. Thus we have barium oxide (or monoxide) BaO, and barium peroxide (or dioxide) BaO_2, magnetic oxide of iron Fe_3O_4, ferrous oxide FeO, and ferric oxide Fe_2O_3. In cases like the last two the terminations *-ous* and *-ic* applied to the *metal* correspond to the smaller and larger proportions of *oxygen*, respectively, which the metal is able to hold in combination.

Many oxides, like those of iron, are almost indifferent to water, but others, like those of sulphur and phosphorus, interact with it readily (see under Water). Some give sour solutions, containing acids dissolved in the excess of water. Such solutions turn blue litmus, a vegetable dye, red. Others give solutions with a taste like soap or borax, and here the dissolved substance is called a base (*q.v.*), and turns litmus blue. Thus sulphur dioxide and phosphoric anhydride give sulphurous acid and phosphoric acid respectively:

$$SO_2 + H_2O \rightleftarrows H_2SO_3$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.*$$

If the product, to whichever class it belongs, is not volatile, it may be obtained by evaporating the excess of water. In the case of sulphurous acid, the above action is reversed by evaporation and the sulphur dioxide and water both pass off; in that of phosphoric acid, the white crystalline acid is obtained. In consequence of their relation to the acid, differing from it in *not* containing the elements of water, these oxides are often called **anhydrides**.

Combustion. — Violent union with oxygen is called in popular language **combustion** or burning. Yet since oxygen is only one of many gaseous substances known to the chemist, and similar vigorous interactions with these gases are common, the term has no scien-

* Here summation of the formulæ on the left would give $H_6P_2O_8$, but in such cases, unless there are reasons to the contrary, the common factor is put in front and the formula reduced to its lowest terms.

tific significance. The union of iron and sulphur, even, gives out light and heat, and is quite similar in the chemical point of view to combustion.

In connection with this, however, it may be worth while to notice the distinction between combustible and incombustible substances. Things which are incombustible may be divided into two classes. There are those substances which already contain all the oxygen which they can hold in combination. Such are the oxides whose formation we observed in the experiments described above. In everyday life, limestone, sand, bricks, and most rocks are illustrations. The other substances ordinarily classed as incombustible are those which do not unite with diluted oxygen, as it is found in the air, with sufficient vigor. The iron used in the construction of fireproof buildings is the commonest example of this class.

Oxidation. — The rusting of metals differs from combustion mainly in speed. Often the products are identical in composition and properties with the oxides formed by combustion. In the case of iron, burning gives us the magnetic oxide (Fe_3O_4), while rusting in cold, moist air yields a hydrated ferric oxide (Fe_2O_3 + Aq*). The products differ in composition, but are closely related.

This process of slow oxidation, although less conspicuous than combustion, is really of greater interest. Thus the decay of wood is simply a process of oxidation whereby the same products are formed as by the more rapid ordinary combustion. Large volumes of pure water are mixed with sewage, the object being, not simply to dilute the latter but to introduce water containing oxygen in solution. This has an oxidizing power like that of oxygen gas, and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. In our own bodies we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen from the air taken into the lungs combines with the hæmoglobin in the red blood-corpuscles. In this form of loose combination, it is carried by the blood throughout our tissues and

* The formula H_2O may not be used excepting to indicate a definite proportion of the elements of water (18 parts). Where the proportion varies according to circumstances, as here and in the case of solutions, the contraction Aq is employed.

is there used for oxidizing waste materials. The carbon dioxide is carried back to the lungs by the blood, and finally reaches the air during exhalation. To supply the place of the material thus removed, we are under the continual necessity of building new tissue from the food which we eat. If we cease to eat, we become lighter and weaker, showing that a real portion of our structure is gradually being consumed by oxidation.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction**.

Means of Altering the Speed of a Given Chemical Action: By Change of Temperature. — That the same change may proceed with very different speeds according to conditions is a familiar fact. For example, **raising the temperature increases the rapidity of all chemical interactions.** Thus, cold iron combines with oxygen very slowly, giving rust, while white-hot iron sheds quantities of scales of an oxide, formed in the few moments that it is under the blacksmith's hammer. White-hot coal unites with oxygen in the air to form carbon dioxide and seems to disappear before our eyes, while in the cellar, even in warm weather, we observe no appreciable diminution in its amount. No temperature can be found, however, at which the interaction definitely begins. We believe that every such change proceeds with *some* speed at every temperature.

If, on bringing two materials together, the chemist observes no marks of chemical action, he immediately begins cautiously to *heat* the mixture. This appeal to the magnifying effect of a rise in temperature is always made as a matter of course.

The common expressions used in chemistry in describing temperatures, along with the corresponding readings of the thermometer, are as follows:

Incipient red heat,	about 525°.	Yellow heat,	about 1100°.
Dark red heat,	" 700°.	Beginning white heat,	" 1300°.
Bright red heat,	" 950°.	White heat,	" 1500°.

Rapid Self-sustaining Chemical Action and Means of Initiating it. — When a piece of wood is set on fire at one end, the heat produced by the action itself raises the temperature of neighboring portions until their speed of union becomes equal to that of the part originally lighted. In this way the whole becomes finally inflamed.

When we blow the blaze out, the great excess of cold air suddenly lowers the temperature of the wood, and of the gas rising from it, and rapid union ceases. Whether a given set of materials can maintain itself at a temperature proper to violent interaction will depend on the amount of heat developed by the action itself on the one hand, and the losses of heat by conduction and radiation on the other. If the latter are great, the former must be greater. Thus the union of iron and oxygen *per se* gives heat enough to warm the materials to the burning temperature and leaves much over for radiation. But iron in air, which is four-fifths nitrogen, can receive the oxygen only one-fifth as fast at the start, and even more slowly as, later, the nitrogen accumulates round it. And besides, all the nitrogen has to be heated to, perhaps, 2000°. The task is too great. The union is impeded and the iron is not oxidized fast enough to generate the heat required to maintain everything at this high temperature. Poor conductors of heat, like wood and candles, fare better. Powdered iron, with its particles presenting large surface to the air relatively to the weight of material in each particle to be heated, burns well.

The initial supply of heat required to *start* a violent chemical action must not be confused with the heat subsequently developed as the action proceeds. The *preliminary supply* varies with circumstances, and may be made as small as we choose by limiting the area first heated and using ordinary precautions against radiation and convection. The heat *produced by the interaction itself*, however, is fixed in amount, and depends only on the materials and their quantity.

Heating is not the only means used to give the initial acceleration to a self-sustaining chemical change. Thus in striking a match a rather violent vibration is employed to hasten the torpid action in a small part of the material, and the heat produced by the resulting action quickly ignites the whole. The same explanation accounts for the explosion of gun-cotton by a percussion fuse.

Other Means of Altering the Speed of a Given Chemical Change: By Catalysis. — When, without any change in temperature, an extra substance increases the speed of a chemical change, seemingly by its mere presence, without itself suffering any permanent change, we call this **catalytic** (Gk. κατά, down; λύσις, the act of loosing) or **contact action.** The word was originally used for cases of

decomposition. The foreign body is called the catalytic or contact agent, and the process catalysis. The effect of manganese dioxide on the decomposition of potassium chlorate (p. 47) is of this nature. When some of the chlorate is placed in a test-tube, provided with a two-hole stopper and delivery tube, and is melted carefully so as to avoid superheating, scarcely any evolution of oxygen can be perceived at this temperature (351°). If now a pinch of pulverized manganese dioxide, hitherto held in one of the holes of the stopper by means of a small plug of glass rodding, be dropped into the molten mass by forcing a longer rod into the hole, the oxygen is given off in torrents in consequence of the enormous acceleration of the decomposition. Yet the manganese dioxide may be recovered unchanged from the residue. Manganese dioxide, of course, will itself give oxygen (p. 46), but the decomposition is hardly noticeable at 400°.

Thermochemistry. — As we have seen, heat is liberated in connection with many chemical changes (pp. 6, 13, 49). Such changes are called **exothermal**. In other chemical changes (pp. 8, 13, 46) heat is continuously absorbed. These are called **endothermal** changes. Since the activities, or affinities of two substances (say, two metals) may often be measured (p. 19) by observing the amounts of heat liberated when each combines with a third substance (say, oxygen), it will be instructive now to consider some of the elementary facts of thermochemistry.

The chemical interactions to be studied thermally are arranged so that they may be carried out in some small vessel which can be placed inside another containing water. The whole apparatus is called a calorimeter. The heat developed raises the temperature of this water. Where gases like oxygen are concerned, a closed bulb of platinum forms the inner vessel. The quantity of heat capable of raising one gram of water one degree in temperature, between 0° and 100° Centigrade, is called a **calorie**. So that 250 grams of water raised 1° would represent 250 calories, and 20 grams of water raised 5° would represent 100 calories.

While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally that represented by the formula of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon with

thirty-two grams of oxygen, and is sufficient to raise nearly 100,000 grams of water one degree. This is expressed as follows:

$$C + 2O \rightarrow CO_2 + 100{,}000 \text{ cal.}$$

In other words, the combustion of less than half an ounce of carbon will raise one kilogram (over two pounds) of water from 0° to the boiling-point.

It is always found that the same quantities of any given chemical substances sustaining the same chemical change under the same conditions produce or absorb, according as the action is exothermal or endothermal, amounts of heat which are equal.

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer will show that a heap of rusting nails is somewhat higher in temperature than surrounding bodies. Poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation. The warmth of our own bodies is in part due to the same cause.

It should be noted that production or absorption of heat is not, in itself, an evidence of chemical action. Physical changes are all likewise accompanied by the same phenomena. Thus, the evaporation of water absorbs heat, and condensation of a vapor and the crystallization of a supercooled liquid liberate heat.

Exercises. — 1. Enumerate other instances, already encountered, of the use of the terminations *ous* and *ic* to distinguish different degrees of oxidation. For what other purposes have the same terminations been used?

2. What difference in composition between potassium chlor*ide* and chlor*ate* are the terminations designed to indicate? Applying the same idea, how would ferrous sulph*ate* (*q.v.*) differ from ferrous sulph*ide*, and cupric sulph*ate* from cupric sulph*ide*?

3. Define and illustrate: density of a gas (p. 48, and see p. 61), specific gravity of a solid or liquid (pp. 2, 23).

4. Enumerate the classes of facts given under the heads of, Physical Properties, and Chemical Properties of oxygen, respectively (see p. 75).

5. Construct the equations for the combustion of phosphorus, carbon, and iron in oxygen (pp. 49, 50).

6. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the formula of the latter, and the equation (p. 41)?

7. Which are the components (p. 22) of the liquid made by treating phosphoric anhydride with water? Which are the constituents (p. 51) of phosphoric acid?

8. How should you show that, in the making of oxygen from a mixture of potassium chlorate and manganese dioxide, the latter remains unchanged? Which properties (p. 23) are you employing for this purpose?

9. The substances, like phosphorus and sulphur, which burn rapidly in ordinary oxygen, combine very, very slowly with oxygen which has been freed from moisture by careful drying. How is this effect of water to be classified?

10. Discuss the union of iron and sulphur (p. 6) and the decomposition of mercuric oxide (p. 7) in their relation to the explanations on pp. 53–54.

11. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from 15° to 37° (p. 55)?

12. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur (p. 55)?

CHAPTER VI

THE MEASUREMENT OF QUANTITY IN GASES

A SPECIMEN of a gas, like a specimen of a solid or a liquid, may be weighed, but it is usually easier to determine the quantity of the gas by (1) measuring its volume, and at the same time (2) noting its temperature on a thermometer suspended in it or close to it, and (3) ascertaining the pressure which it exercises.

The Measurement of the Pressure of a Gas. — In almost all cases the easiest way to take account of the pressure of a gas is to place it in an apparatus so constructed that one boundary of the volume is a liquid. The apparatus is then so adjusted that the surface of the liquid in contact with the gas is *at the same level* as the *free* surface of the liquid which is exposed to the atmosphere. The equality in the levels of the liquids is then a guarantee that the specimen of gas and the atmosphere are exercising equal pressures on the liquid. At this stage the volume of the gas is measured, and simultaneously the pressure of the atmosphere and, therefore, of the gas, is ascertained by reading the barometer.

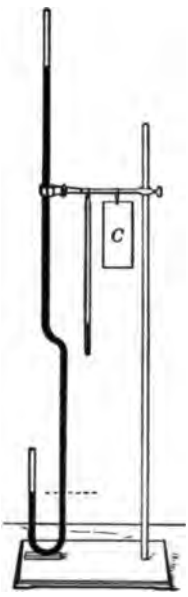

FIG. 19.

The barometer (Fig. 19) consists of a bent tube containing mercury. The short limb (to the left) is open and the pressure of the atmosphere is exercised on the surface of the mercury there. The longer limb (to the right) is closed at the top and in it there is no gas above the mercury. When the tube is inclined, the surface of the mercury in the longer limb endeavors to retain the same vertical height above the lower surface and consequently rises, and, with sufficient

inclination, will reach entirely to the top of the tube. The downward pressure of the mercury on the right, above the dotted line, is exactly equal to the pressure of the atmosphere on the free surface of the mercury at the same level. The amount of the latter pressure is proportional to the length of the column of mercury above the dotted line. Hence, reading the height at which the mercury stands above the free surface gives us a measure of the pressure of the atmosphere and of any specimen of gas which is at the same pressure.

This is called the *uncorrected* reading. It is immediately reduced to the reading which would have been made if the barometer and its mercury had been at 0° (*corrected reading*), by noting the temperature on the adjacent thermometer and subtracting from the uncorrected reading the necessary *correction* (Table of corrections, *C*, Fig. 19).

For example: the volume of gas, after adjustment to atmospheric pressure, is 200 c.c. and its temperature 17°. The uncorrected barometric reading is 744 mm. with the barometer (perhaps in a different room from the gas) at 15°. The correction is − 2.0 mm. The corrected reading is therefore 742 mm.

Finally, since the atmospheric pressure varies from day to day, the volume at the observed pressure is corrected to that which the same quantity of gas would have occupied at the standard pressure of 760 mm. of mercury. By careful measurements, **Boyle** (1660) found that **the volumes occupied by the same sample of any gas are inversely proportional to the pressures at each volume.**

The illustration just given will show how this additional correction is applied. There were 200 c.c. of the gas at 17° and 742 mm. (corr.). The question is: What would be the volume of this amount of gas at 760 mm.? At this new pressure (760 mm.) which is greater than the old pressure (742 mm.), the volume will become *less*. Hence we change the volume in the proportion of these pressures, *placing the smaller number in the numerator*, so as to get a smaller volume as the answer: $200 \times \frac{742}{760}$ = volume at 760 mm., = 195.3 c.c. If we wished to convert 100 c.c. at 775 mm. to 760 mm., we should reason that the new pressure was smaller, and the volume would become greater, and should therefore place the larger number (775) in the numerator so as to get a larger volume for the answer.

The Correction of the Volume of a Gas for Temperature.— The same sample of gas will occupy, when heated, a larger volume, and when cold, a smaller volume than before. The change in volume

for each degree Centigrade is $\frac{1}{273}$ of the volume of the same sample at 0°. To simplify the calculation we begin by converting the temperature to the absolute scale by adding 273° to each temperature: **The volumes assumed by a sample of gas at different temperatures, the pressure remaining constant, are in the same proportion as the corresponding absolute temperatures (Charles, 1787).** If the volume remains constant, then the pressure changes in the same proportion.

In the illustration used above, there were 200 c.c. of gas at 17°, and it is required to know the volume at 0°. We add 273 algebraically to each temperature, and the question becomes: There are 200 c.c. of gas at 290° Abs., what will be its volume at 273° Abs.? The volume changes in the direct ratio of the temperatures. The new temperature is *lower* than the old, and the new volume will therefore be smaller than the old. Then $200 \times \frac{273}{290}$ = volume at 0° (273° Abs.) = 188.27 c.c.

The above laws are usually applied to any example simultaneously. Thus, 200 c.c. of gas at 742 mm. pressure (corr.) and 17° become $200 \times \frac{742}{760} \times \frac{273}{290}$ = 183.8 c.c. at 0° and 760 mm.

Mixed Gases: Aqueous Tension. — Two gases at the same temperature, provided they do not interact chemically, do not interfere with each other's pressures when mixed. Thus, if they are forced into the same volume, the pressure of the mixture is equal to the sum of those of the components (Dalton's law, 1807). The gases are therefore still thought of individually, and the share which each gas has in the total pressure is called its **partial pressure**. This, like any other gaseous pressure, is proportional to the concentration of the particular gas in the mixture.

For example, a gas measured over water contains water vapor. The partial pressure of this, called the **aqueous tension** (*q.v.*), which is definite for each temperature, must be subtracted from the total pressure. The remainder is the partial pressure of the gas being measured, and this remainder is used as the pressure of this gas in any calculation. Thus, in a gas measured over water at 22°, the total pressure includes 19.7 mm. (the aqueous tension at 22°) pressure of water vapor. Hence 150 c.c. of gas over water at 22° and 750 mm. is the same in amount as 150 c.c. of the same gas in dry condition at 22° and 730.3 mm. (there being simply 150 c.c. of water vapor at 19.7 mm. mixed with it). To obtain the volume of dry gas at 0° and 760 mm. we have the expression $150 \times \frac{273}{295} \times \frac{730.3}{760}$.

Densities of Gases.* — The **density** of a gas is the mass of 1 c.c. of the gas at 0° and 760 mm. pressure. Sometimes the weight of one liter (1000 c.c.) is called the density. Often the relative weight of the gas, the weight of an equal volume of air, or oxygen, or hydrogen being taken as unity, receives the same name.

FIG. 20.

The most direct method of measuring the density of a gas is to employ a light flask provided with a rubber stopper and stopcock (Fig. 20). By means of an air-pump the contents of the flask are removed, and it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, represents the volume of the content of the flask in cubic centimeters. This volume is reduced to 0° and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at 17° and 742 mm. The weight of the gas is found to be 0.26 g. We ascertained (p. 60) by calculation that at 0° and 760 mm. this volume would be 183.8 c.c. The weight of a liter is given by the proportion $183.8 : 0.26 :: 1000 : x$. Here $x = 1.415$ g. When the operation is performed carefully, and the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly approaching the exact one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we

* The subjects of this section are not actually used until Chapter xii (on Molar Weights) is reached.

must divide the answer by the weight of a liter of hydrogen (0.08987 g.). In the above case the quotient is 15.74. The accepted value is 15.90. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at 0° and 760 mm. pressure.

By using a modification of the flask just described, it is possible to ascertain the weights of known volumes of the vapors of liquids and solids. A temperature sufficiently high to vaporize the substance must be employed. The volume is reduced by rule to 0° and 760 mm. and the density (in this case known as the **vapor density**) is calculated as before. The reduction to 0° and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before 0° was reached, if the cooling were actually carried out. But the value for the density *as it would be* at 0° and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

Exercises. — The foregoing cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at 15° and 750 mm. to 0° and 760 mm.
2. Reduce 110 c.c. of gas at − 5° and 741 mm. to 0° and 760 mm.
3. Convert 500 c.c. of gas at 25° and 700 mm. to 18° and 745 mm.
4. Reduce 250 c.c. of gas (standing over water) at 22° and 755 mm. to the dry condition and to 0° and 760 mm.
5. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at 20° and 752 mm.?

CHAPTER VII

HYDROGEN

In each chapter dealing with the chemistry of some substance the same topics are always discussed in the same order, namely, History, Occurrence, Preparation, Physical properties, and Chemical properties. Additional sections dealing with special topics are inserted when necessary.

The independent nature of hydrogen was first established by Cavendish in 1766. Somewhat later (1781), he showed that hydrogen when it burned gave water vapor. Taken in conjunction with Lavoisier's proof that oxygen was the active substance in the air (1777), this fact showed that water was a compound of hydrogen (Gk. ὕδωρ, water; γάννᾶν, to produce) and oxygen.

Occurrence. — The free element is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. The air contains not more than one part in 30,000. Its lines are very prominent in the spectra of the sun and of most stars.

In combination, it constitutes about 11 per cent of water. It is an essential constituent of all acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, and all animal and vegetable bodies.

Acids. — In making hydrogen, the acids are used almost exclusively. The common acids are hydrochloric acid (HCl, Aq), and sulphuric acid (H_2SO_4, Aq). The usual forms are mixtures containing water, the variable amount of the latter being indicated by the symbol Aq. The former is a solution of a gas, hydrogen chloride. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (39 per cent by weight) as the water can dissolve. The "commercial" acid contains impurities and is also less concentrated. The "concentrated" sulphuric acid is an oily liquid containing practically no water. The "commer-

cial " sulphuric acid contains 6 to 7 per cent of water, besides impurities. Acetic acid ($HC_2H_3O_2$, Aq) is a solution of a liquid in water. All the " dilute " acids contain 70 to 80 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the equations.

The name " acid " is restricted to one class of substances having certain definite characteristics. Hydrogen is the one essential constituent of all acids. Their aqueous solutions have a sour taste and change the color of litmus from blue to red. When free from water they do not conduct electricity. When dissolved in water they conduct, and are decomposed by the electric current, and their hydrogen (or one unit weight of it in the case of acetic acid) is displaced by certain metals.

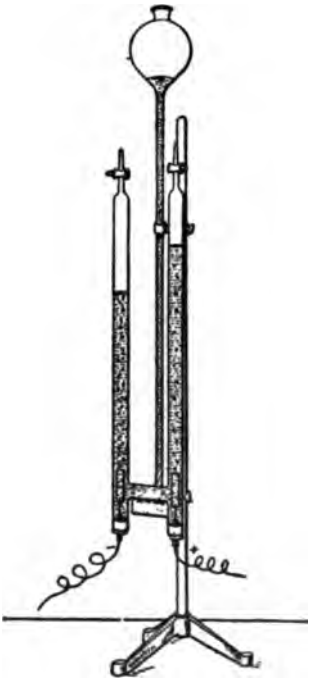

FIG. 21.

In describing the chemical behavior of acids, we speak of the hydrogen as the **positive radical**, because in electrolysis it is attracted to the negative pole, and of the material combined with the hydrogen as the **negative radical** because it is attracted to the positive pole. Thus the negative radicals in the above acids are Cl, SO_4, and $C_2H_3O_2$, respectively. The first (Cl) is a simple radical, the others compound. In many interactions the compound radicals move as units from one state of combination to another.

Preparation of Hydrogen by Electrolysis. — If we dissolve *any acid* in water, and immerse the wires from a battery in the solution, bubbles of hydrogen begin to appear on the *negative* wire (the cathode) and rise to the surface. All the other constituents, whatever they may be, are attracted to the positive wire (the anode) and are set free in some form at its surface. An apparatus devised by

Hofmann (Fig. 21) enables us to secure the hydrogen, which ascends on the left and accumulates at the top of the tube, displacing the solution. The other products, if gaseous, occupy a separate tube on the right side. In a typical case the production of hydrogen ceases when the acid is all decomposed. The water alone is an almost complete nonconductor, so that the flow of the electricity practically ceases at the same time. Thus when hydrochloric acid is used: $HCl \rightarrow H$ (neg. wire) $+ Cl$ (pos. wire), and the chlorine, a soluble gas, remains dissolved in the water near one pole (see Electrolysis).

Preparation of Hydrogen by Displacement from Diluted Acids. — Certain metals, like zinc, iron, and aluminium, when placed in a dilute acid, combine with the radical of the acid and so liberate the hydrogen. The acids *must be diluted with water* before rapid action occurs. The hydrogen escapes in bubbles, and evaporation of the remaining liquid gives in dry form the compound of the metal with the other constituents of the acid. Thus, with zinc and sulphuric acid, zinc sulphate is produced:

$$Zn + H_2SO_4 \rightarrow 2H + ZnSO_4;$$

and with tin or aluminium and hydrochloric acid we get stannous chloride or aluminium chloride:

$$\underset{\text{(Tin)}}{Sn} + 2HCl \rightarrow 2H + \underset{\text{(Stannous chloride)}}{SnCl_2},$$

$$Al + 3HCl \rightarrow 3H + AlCl_3.$$

FIG. 22.

The water undergoes no change during the action, although its presence is essential. It is simply a part of the apparatus. Any acid may be used, although with many the action goes on very slowly. In all cases the plan of the action is the same: the metal is said to *displace* the hydrogen (see below).

With a Kipp's apparatus (Fig. 22) the gas may be made on a large scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above, so that the action ceases. Yet the action is ready to begin again the moment any portion of the stored gas is drawn off for use.

A rather sharp line can be drawn between those metals which displace hydrogen from dilute acids and those which, like mercury, silver, and gold, do not (see Electromotive series, also footnote to p. 24). Contact of the zinc or iron with an inactive metal, like platinum, forms an electrical couple and hastens the interaction.

Preparation of Hydrogen from Water. — When sodium, one of the constituents of common salt, is thrown upon water, the metal gradually disappears and hydrogen is liberated with violent effervescence. Every one of the metals which act on dilute acids will displace hydrogen from water, and no others will do so. The more active metals, like potassium and sodium, which would act with uncontrollable vigor on dilute acids, displace the hydrogen *rapidly* from *cold* water. Magnesium and zinc show obvious action on water at 100° only, and are much assisted by contact with another metal.

In all cases in which cold or boiling **water** is employed, the hydrogen of the water is not completely displaced. The metal forms an hydroxide, such as sodium hydroxide or magnesium hydroxide:

$$Na + H_2O \rightarrow H + NaOH,$$
$$Mg + 2H_2O \rightarrow 2H + Mg(OH)_2.$$

With sodium the resulting solution has a soapy feeling and turns litmus from red to blue, a color reaction which is the precise opposite of that of acids (p. 51). Substances causing these two effects are called *alkalies*, and the soapy feeling and the action on litmus are **tests** for alkalies. Evaporation reveals the sodium hydroxide, the alkali, as a white solid.

With **steam** at a red heat, metals like iron, zinc, and magnesium interact vigorously. The steam, generated in a flask, enters at one end of the tube containing the metal (Fig. 23), and the hydrogen passes off at the other. Since, at a red heat, all hydroxides, except those of potassium and sodium, are decomposed into an oxide of the

metal and water, as, for example, $Mg(OH)_2 \rightarrow MgO + H_2O$, the *oxides* are formed in this case:

$$Mg + H_2O \rightarrow MgO + 2H.$$

Iron gives the magnetic oxide, Fe_3O_4. We note that, to make this

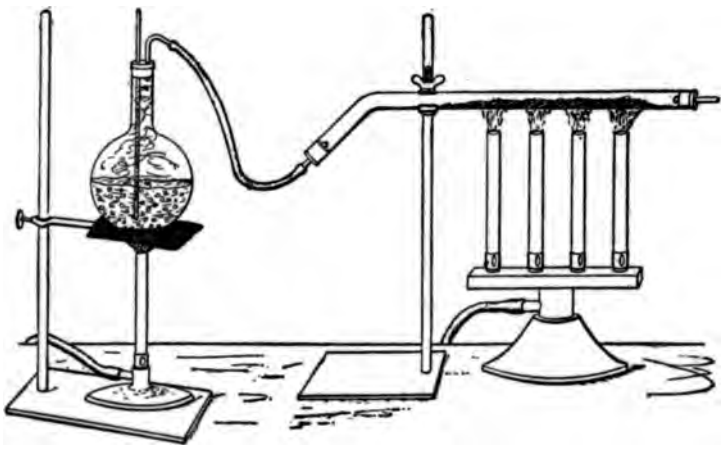

FIG. 23.

substance (pp. 41–42), four unit-weights of oxygen, and therefore four formula-weights of water, are required:

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 8H.$$

The Other Ways of Preparing Hydrogen. — For special purposes, hydrogen may be made by boiling an aqueous solution of sodium hydroxide with aluminium turnings, when sodium aluminate is formed: $Al + NaOH + H_2O \rightarrow NaAlO_2 + 3H$; also by heating powdered zinc and dry sodium hydroxide, the product being sodium zincate: $Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H$.

Preparation of Simple Substances. — There are two general ways of obtaining simple substances, both of which have now been illustrated. If the element occurs uncombined in nature, as oxygen, sulphur, and gold do, it is only necessary to free it from foreign materials (impurities) with which it is mixed. If no such supply exists, as in the case of hydrogen, or if the purification is difficult,

then some compound, natural or artificial, is decomposed and the element liberated.

The liberation, in turn, may be effected in two ways. The compound may (1) be forced apart by the application of energy, usually in the form of heat, as with some compounds of oxygen (p. 46), or electricity, as in the liberation of hydrogen and metals by electrolysis. Or (2) the desired constituent may be liberated, as in the case of hydrogen, by offering to the other constituents some substance with which they will unite.

Displacement. — We now have before us illustrations of two sub-varieties of the third kind (p. 10. See footnote to p. 24) of chemical change, the one in which compounds are *decomposed* and the parts *combine* in a new way. The first sub-variety was *double decomposition*, as in the action of sodium chloride upon silver nitrate:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3.$$

In that class of cases *two compounds* interact, each splits into the radicals of which it is composed, and *two new compounds* are formed by union of the radicals crosswise. The actions just used in the preparation of hydrogen differ from these, inasmuch as **one compound and one element interact, the compound splits into its radicals, and one compound and one free element are produced:**

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H,$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H.$$

The interacting element, here the zinc, is said to **displace** the other, here the hydrogen, from combination. In double decomposition there is an *even exchange*, the sodium, for example, giving up one radical (Cl), and getting another (NO_3). In displacement one element gains a radical while another loses it, the zinc, for example, giving up nothing but getting SO_4, while the hydrogen loses SO_4, and gains nothing in return.

Valence.* — We shall gain much help in the making of equations if we now introduce and bring into relation to the symbols a conception for which the remarks about atomic weights (p. 36) have paved the way. It will have been observed that the composition of the

* If desired, the sections on Valence may be taken up equally well after the remaining sections of this chapter have been studied.

chlorides of aluminium, tin, and sodium are represented by the formulæ $AlCl_3$, $SnCl_2$, and NaCl, respectively. Again, the hydroxide of sodium is NaOH, while those of magnesium and calcium are $Mg(OH)_2$ and $Ca(OH)_2$. In making equations we constantly need to know whether the chloride of an element, say magnesium, is MgCl, or $MgCl_2$, or $MgCl_3$, or $MgCl_4$, etc., and whether its sulphate is $MgSO_4$, or Mg_2SO_4, or some other combination of the symbols. To answer questions like this it is not necessary to know the formula of every compound of each element: the apparent disorder of these numbers can be reduced to rule, and the reader should endeavor thoroughly to master the rule before going farther.

If the method by which the atomic weights were derived from equivalents (p. 32) is now reëxamined, the nature of this rule will be seen. It was found, for example, that 9.03 parts of aluminium (p. 36) combined with the equivalent weights of the other elements, and therefore with 35.45 parts of chlorine. If this weight of aluminium had been accepted as the final unit (the atomic weight), then it would have been represented by the symbol Al, and, since Cl stands for 35.45 parts of chlorine, the formula of the chloride would have been AlCl. In point of fact, however, a number three times as large as the equivalent, namely, 27.1, was chosen as the atomic weight of aluminium, and the symbol Al stands for this triple quantity. If the equivalent of chlorine had also been tripled in making its atomic weight, the amounts represented by the symbols would still have been chemically equivalent, and the formula would still have been AlCl. But the equivalent of chlorine was left unaltered. Hence, to get the equivalent amounts (*i.e.*, the actual combining quantities) of the two elements, we must have 3Cl with 1Al. The formula is thus $AlCl_3$. Now, it is evident that this tripling of the equivalent of aluminium will affect the formulæ of *all* its compounds. Whenever it is combined with an element which, like chlorine, has identical equivalent and atomic weights, the formula of the compound will be of the form AlX_3. In accordance with this we have the bromide $AlBr_3$. In making the formulæ of compounds of aluminium, the chief thing to be kept in mind, therefore, is the fact that its atomic weight contains three equivalents and always combines with three equivalents of another element. This fact we state by saying that the **valence** of the atomic weight of aluminium is three, or simply **that the element aluminium is trivalent.**

Similarly, the equivalent of tin is 59.5 and its atomic weight is 119. This atomic weight therefore contains two equivalents of tin and combines with two equivalents of any other element. Hence, the formula of a compound of tin with an element of the chlorine class will be SnX_2. Thus tin is **bivalent**. In like manner the equivalent of sodium is 23, and this number was not altered in making the atomic weight. Hence, the symbol Na stands for one equivalent, and the formula of the compound with chlorine is NaCl. Elements whose atomic weights are identical with their equivalents are described as **univalent**.

Thus **the valence of an element** may be defined **as the number of equivalent weights contained in its atomic weight.** Arithmetically it is the integer by which the equivalent weight was multiplied in forming the atomic weight. The above explanation shows that we may define the **valence of an element** also as **the number of atomic weights of a univalent element, with which its atomic weight will combine.**

Sometimes the valence is indicated in the symbol thus: Al^{III}, Sn^{II}, Na^{I}, Cl^{I}, Br^{I}. The table of atomic weights (p. 36) shows the following additional cases: O^{II}, Cu^{II}, S^{II}, Hg^{II}, H^{I}, Fe^{II}, Mg^{II}, C^{IV}. With the help of this list the formulæ of compounds may easily be made. Thus, oxygen is bivalent, and an atomic weight of oxygen, represented by O, will combine with two atomic weights of a univalent element as in $O^{II}H_2^{I}$ (water), or with one atomic weight of a bivalent element as in $O^{II}Sn^{II}$ (stannous oxide), $O^{II}Hg^{II}$ (mercuric oxide), $O^{II}Cu^{II}$ (cupric oxide), $O^{II}Mg^{II}$ (magnesium oxide). Again, carbon being quadrivalent, the atomic weight combines with four units of chlorine and of hydrogen in $C^{IV}Cl_4^{I}$ (carbon tetrachloride) and $C^{IV}H_4^{I}$ (methane), or with two units of oxygen and of sulphur in $C^{IV}O_2^{II}$ (carbon dioxide) and $C^{IV}S_2^{II}$ (carbon disulphide). When it combines with a trivalent element, equal numbers of equivalents of each element must be used, as in $C_3^{IV}Al_4^{III}$ (aluminium carbide), where C_3 and Al_4 contain twelve equivalents each. This method, with a very few exceptions, will give the formulæ of all compounds containing only two elements — so-called **binary compounds**.

The Valence of Radicals. — The valence of elements can easily be determined when they are present in *binary* combination. This is no longer the case when more than two elements are united together.

A study of chemical changes shows, however, that even here the conception of valence can still be employed. In the interaction of zinc with dilute sulphuric acid:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

the group SO_4 passes as a whole from combination with 2H to combination with Zn. Hence, although we cannot by inspection determine the valence of sulphur, we do perceive that the radical SO_4, as a whole, must be bivalent. It occurs, in fact, in all sulphates, as Ag_2SO_4, $MgSO_4$, and $Al_2(SO_4)_3$, and in the interactions of these substances it usually passes intact from one state of combination to another, and behaves as if it were a unit of a single element of valence two. Again, in the interaction of salt with silver nitrate (p. 40), we observe that the radical NO_3 is univalent. Still again, the compositions of the compounds $CaCl_2$ and $Ca(OH)_2$ show that the radical OH (hydroxyl) is univalent. The formula NaOH leads to the same conclusion.

This addition to our ideas enables us greatly to extend the list of substances of which we can write the formulæ. Thus, the hydroxides all contain $(OH)^{I}$, *e.g.* $Al^{III}(OH)_3^{I}$ (aluminium hydroxide), $Sn^{II}(OH)_2^{I}$ (stannous hydroxide), $Cu^{II}(OH)_2^{I}$ (cupric hydroxide). The nitrates all contain $(NO_3)^{I}$, as: $H^{I}(NO_3)^{I}$(nitric acid), $Mg^{II}(NO_3)_2^{I}$ (magnesium nitrate).

It is to preserve the identity of the radicals that we write them in brackets and place the coefficient outside, as $Ca(OH)_2$ and $Mg(NO_3)_2$, instead of using the forms CaO_2H_2, MgN_2O_6, and so forth. In fact, substances which commonly interact as if the radicals were single elements, we regard as binary compounds.

In writing formulæ of inorganic compounds we usually place the positive radical (p. 64) in front and the negative radical after it.

How to Ascertain the Valence of an Element or Radical. — The above shows that the valence of one element or radical may always be ascertained by examination of the formula of a compound containing another element or radical of known valence. Thus, when we know the formula of sodium iodide to be $Na^{I}I$, or that of hydrogen iodide to be $H^{I}I$, we infer that iodine is univalent. The formula of silica (sand) SiO_2^{II} shows silicon to be quadrivalent, and indicates that the chloride must be $SiCl_4$. Similarly the formula of

calcium carbonate $Ca^{II}CO_3$ shows that the radical CO_3, which is common to all carbonates, must be bivalent. Hence, **the chemist** does not memorize the valences themselves; he **recovers the valence of an element or radical, when needed, by recalling the formula of a substance containing this element or radical in combination with a more familiar element or radical,** such as Cl^I or H^I.

It is absolutely essential that correct valences should be used in constructing equations, and, at first, the student will find the task by no means easy. He should give special attention to this matter until, by solving the exercises at the end of this chapter, and by careful examination of all the equations encountered in the text, he has mastered the subject.

Multiple Valence. — Some elements show more than one valence. This is as much as to say that an atomic weight of such an element may form stable compounds with two, or even more different numbers of equivalents of another element. This fact has already been mentioned, for it is implied in the law of multiple proportions (p. 33). Thus an atomic weight of tin may form two different compounds with chlorine, namely, $Sn^{II}Cl_2$ (stann*ous* chloride) and $Sn^{IV}Cl_4$ (stann*ic* chloride). Tin behaves in the same way towards other elements, however, and we have a *series* of stann*ous* compounds, SnO, $SnBr_2$, and so forth, and a corresponding series of stann*ic* compounds, SnO_2, $SnBr_4$, etc. Two different valences of the same element or radical gives rise therefore to two complete sets of compounds. The nomenclature used to distinguish the two series has been discussed before (p. 51). As a rule, an element passes from one form of combination to another without change of valence. But compounds of elements like tin can also undergo changes in course of which the valence alters.

Physical Properties of Hydrogen. — Some of these may be given in tabular form:

Colorless	Boiling-point, − 252.5°
Tasteless and Odorless	Melting-point (58 mm.), − 260°
Wt. of 1 l., 0.08987 g.	Sol'ty in Aq, 1.9 vols. in 100 (14°)

Air is 14.5 times as heavy, hence the gas may be poured upwards and is used for filling balloons. A liter flask filled with air requires

about 1.2 g. to be added to the tare to restore the balance when the air is displaced by hydrogen. Hydrogen was first liquefied in visible amounts by Dewar (1898). The liquid is colorless, and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid. All other gases except helium (*q.v.*) solidify easily when led into a vessel surrounded by liquid hydrogen.

Hydrogen is absorbed, for the most part in a purely mechanical way, by many metals. Heated iron will take up 19 times its volume of hydrogen, gold takes up 46 volumes, platinum in fine powder 50 volumes, palladium 502 volumes, and silver none. The maximum absorbed by palladium under favorable conditions is 873 volumes.

Diffusion. — If a volume of gas is inclosed at one end of a cylinder, the rest of which is entirely empty, and is suddenly released from this confinement, it spreads with extreme speed so as to occupy the whole of the cylinder to an equal degree. This spreading is not an effect of gravitation, since it takes place upwards or downwards with equal celerity. The same phenomenon is observed when, in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The motion, as this instance shows, takes place through a space occupied by another gas more slowly than, but just as surely as, when the space is empty. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call **diffusion.** It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

Fig. 24.

The different rates of diffusion of different gases are easily shown by comparing their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The porous cylinder *A* (Fig. 24) contains air and is connected with a wide tube which dips beneath the surface of the water. When a cylinder *H* containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the cylinder of hydro-

gen approached it, the air was moving both outwards and inwards through the porcelain, but, being the same air, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and air it is in the ratio $\sqrt{1} : \sqrt{.0695}$, or 3.8 : 1.

Chemical Properties of Hydrogen. — Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel held over the almost invisible blue flame condenses to droplets of water the steam that is produced. Although the flame gives little light, it is exceedingly hot. Platinum melts in it easily. In a closed space it produces a temperature of over 2500°. When hydrogen and oxygen are mingled in a suitable burner, and the flame is allowed to play on a piece of quicklime, the latter becomes white-hot at the spot where the flame meets it. This result is called a **calcium light** or **lime light.**

When hydrogen and oxygen are mixed, the chemical action is very slow at ordinary temperatures, *no perceptible amount of union occurring in a period of five years.* If the mixture is sealed up and kept at 300°, after several days a small part is found to have combined to form water. At 518°, hours are required before the union is complete. At 700° the combination is almost instantaneous. Hence contact with a body at a bright-red heat (p. 53) is required actually to explode the mixture.

Finely divided platinum, when held in the cold mixture, hastens the union (otherwise vanishingly slow) in the part of the gases in contact with it. The heat of the union raises the temperature of neighboring portions and causes explosion of the mass. The platinum is simply a catalytic agent (p. 54) and remains itself unaffected.

Hydrogen unites directly with a minority only of the simple substances. It combines rapidly with oxygen, chlorine, fluorine, and lithium, and more slowly with a few others.

When these elements, especially the first two, are already in combination, hydrogen may still sometimes displace the material with which they are united. Thus, when any one of the oxides of iron is heated in a tube through which hydrogen flows, the latter combines with the oxygen to form water, and the metal is liberated. The skeleton equation (p. 42) is: $Fe_3O_4 + H \rightarrow H_2O + Fe$. We then reason that Fe_3 will give 3Fe. Since all the oxygen is removed from the compound, O_4 will give $4H_2O$. To produce this, 8H is required. Hence:

$$Fe_3O_4 + 8H \rightarrow 4H_2O + 3Fe.$$

This interaction is classed as a displacement. In describing it the chemist would also say that the hydrogen has been *oxidized* and that the oxide of the metal has been *reduced* (pp. 52–53).

Specific Chemical Properties. — If the foregoing section on the chemical properties of hydrogen and the corresponding section under oxygen (p. 48) are now reëxamined, the nature of the facts contained in, and to be learned from such a section will be seen. Under this head we describe the chemical behavior of a substance, (1) enumerating the other substances, simple or compound, with which it unites or interacts, (2) stating the conditions peculiar to each action, and (3) estimating the intensity of the tendency to chemical change in each case. In the case of a simple substance like oxygen we note particularly with how many of the other elements it can form compounds, how far it unites with them directly, and in how many cases the compounds have to be made by indirect means. In general, we call those simple substances **active** which unite with many other simple substances and do so by direct union. Oxygen, for example, is active, and nitrogen (*q.v.*) is relatively inert.

The Speed of Chemical Actions: a Means of Measuring Activity. — One means of measuring the relative chemical activities of several substances is to observe the speed with which they undergo the same chemical change (p. 19). Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is thus much more active than

zinc. The comparison must be made with such precautions, however, as will make it certain that the conditions under which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during the experiment, for all actions become more rapid when the temperature rises (p. 53). Again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by a study of other similar actions. A single table suffices, therefore, for all purposes (see Electromotive series, also footnote to p. 24).

Exercises. — 1. What are the valences of the negative radicals of phosphoric acid (p. 51), and of acetic acid (p. 64)? What must be the formulæ of calcium phosphate, cupric acetate, aluminium phosphate, ferrous carbonate, ferrous sulphate, cupric chloride?

2. What is the valence of phosphorus in phosphoric anhydride (p. 51)? What must be the formulæ of, (*a*) the corresponding chloride and sulphide of phosphorus, and (*b*) of aluminium oxide?

3. What are the valences of the elements in the following: LiH, NH_3, SeH_2, BN?

4. What are the valences of the metals and radicals in the following: $Pb(NO_3)_2$, $Ce(SO_4)_2$, KCl, $KMnO_4$ (potassium permanganate)? Name all the substances in 3 and 4.

5. Write the formulæ of ferrous and ferric oxides, of ferrous and ferric nitrates, of stannous and stannic sulphides.

6. Make equations to represent, (*a*) the reduction of lead dioxide (PbO_2) by hydrogen, (*b*) the actions of aluminium upon cold water and, (*c*) upon steam at a red heat.

CHAPTER VIII

WATER

THE great quantity of water which occurs in nature makes it one of the most familiar chemical substances. Water is found also in the bodies of both animals and plants in large amounts, and is indeed essential to the working of living organisms.

Natural Waters. — Sea-water holds about 3.6 per cent of solid matter in solution. Rain-water is the purest natural water, but contains nitrogen, oxygen, and carbon dioxide dissolved from the air. Well-waters often contain calcium sulphate, calcium bicarbonate, and compounds of magnesium in solution, and are then described as **hard**. Other waters contain compounds of iron, and still others are effervescent and give off carbon dioxide. These are called mineral waters. All of the dissolved substances are obtained by the water in its progress over or under the surface of the ground.

Water which is to be used for domestic purposes is examined, particularly, for organic matter. This usually gains access to the water by admixture of sewage (p. 52). It is not this organic matter itself which is deleterious, but the bacteria of putrefaction and disease and their products (ptomaines) which are likely to accompany it.

Purification of Water. — The foreign materials which water may contain are divisible into two kinds, — dissolved matter and suspended matter. No water is free from either of these varieties of impurity. In chemical laboratories distilled water is always employed. Yet it is difficult to keep the liquid pure even for a short time. Ordinary glass dissolves in water to a very noticeable extent.

For ordinary purposes the **suspended** matter which water contains is removed by **filtration** (p. 7). In the laboratory this takes place through unsized paper. The pores of the paper are sufficiently small to retain suspended particles, while permitting the passage of the water *with its dissolved matter*. On a large scale, beds of gravel are

employed. In the household, the Pasteur filter is more compact and efficient. The water is forced by its own pressure through the pores of a closed tube made of unglazed porcelain. Care must be taken to clean these tubes at frequent intervals, so that organic and perhaps putrescent matters may not accumulate upon them.

Matter in **solution** cannot be removed by ordinary filtration, and is eliminated by **distillation** (p. 26). Since the water is converted into steam and is condensed in platinum or tin pipes, only gases or volatile liquids dissolved in it can pass into the distillate.

Physical Properties of Water. — A deep layer of water has a blue or greenish-blue color. At a pressure of 760 mm., water exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that its physical properties, discussed below, should be studied attentively. Then too, what is said of water is in general true of all other liquids, from which it differs only in details.

Ice. — The raising or lowering of the temperature of a gram of water through one degree involves the addition or removal of one calorie of heat. The conversion, however, of a gram of water at 0° to a gram of ice at 0° requires the removal of 79 calories. The mere melting of a gram of ice causes an absorption of heat to the same amount, called the **heat of fusion of ice**. At 0° a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends permanently to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice respectively. This temperature is called the **melting** or the **freezing point**. **A temperature**, like this, **at which a substance passes from one physical state of aggregation to another** is called a **transition point**.

Steam and Aqueous Tension. — At atmospheric pressure, water passes into steam rapidly at 100°, but at lower temperatures, and even when frozen, it does the same thing more slowly. The quantity of the vapor present is defined by the gaseous pressure it exercises, the value being called the **vapor pressure** of water vapor (or of the vapor of any other volatile substance) in the location in question.

The most significant fact about vapor pressure is that, *when excess of the liquid is present*, the pressure of the vapor quickly reaches a

definite maximum value for each temperature. In the absence of excess of the water, less than this maximum pressure may exist. More than the maximum pressure proper to a given temperature, if produced by compression, cannot be maintained, for a part of the vapor condenses to the liquid state. The magnitude of this maximum vapor pressure, at a given temperature, depends on the ability of the particular liquid to generate vapor. This maximum vapor pressure is held, therefore, to represent the **vapor tension of the liquid,** at the given temperature, and this is a specific property of the substance.

The vapor tension may be shown by allowing a few drops of water to ascend into a barometric vacuum (Fig. 25). The tube on the left shows the mercury when nothing presses on its surface. The tube on the right shows the result of admitting the water. The difference in the height of the two columns gives the value of the vapor pressure of the water vapor. With excess of water, the value is that of the vapor tension, called, in the case of water, the **aqueous tension.** The jacket surrounding the tube on the right enables us, by adding ice or warm water, to maintain any temperature between 0° and 100°. When ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.5 mm. The vapor pressure of the ice takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at 10° causes a fall of 9.1 mm. and at 20° of 17.4 mm., so that these represent the mercury-height values of the aqueous tension at these temperatures. The quantity of water used makes no difference, so long as *a little more* is present than is required to fill the available space with vapor. With ether, instead of water, at 10° the fall is 28.7 mm.

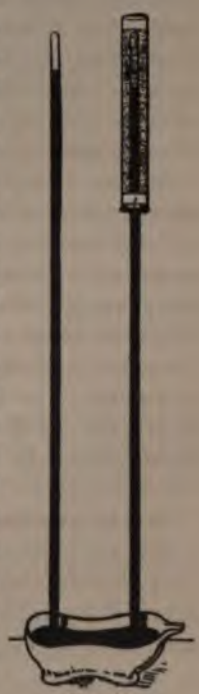

Fig. 25.

With water at higher temperatures the fall of the mercury column becomes much greater. At 50° it is 92 mm., at 70° it is 233.3 mm., at 90° it is 525.5 mm., and at 100° it is 760

mm., or one atmosphere. At 121° the aqueous tension is two atmospheres, at 180° it is ten atmospheres.

When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That **concentration** of vapor which constitutes saturation varies with the temperature of the water and depends therefore solely on the power of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain (p. 60, also pp. 90–91. See footnote to p. 24).

The space immediately above the surface of the ground, which is mainly occupied by atmospheric air, is, on an average, less than two-thirds saturated with water vapor. That is to say, such air, when inclosed in a vessel containing water, will take up about one-half more than it already contains. The vapor of water at 100° in an open vessel displaces the air entirely, and, if the required heat is furnished, the liquid boils. This temperature, like the freezing-point, is a transition point.

A gram of water at 100°, in turning into a gram of steam at 100°, takes up 537 calories. This is called its **heat of vaporization.** Steam, in fact, contains much more internal energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice.

All our substances and apparatus have traces of water, derived from the atmosphere, **condensed on their surfaces.** This water is, in a sense, in an abnormal condition, for it does not evaporate even in dry air. It is observed to pass off in vapor, however, when we have occasion to heat the substance or apparatus.

Water as a Solvent. — One of those physical properties of water which are most used in chemical work is its tendency to dissolve many substances. This subject is so important and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

Chemical Properties of Water. — Water is so very frequently used in chemical experiments in which it is a mere mechanical adjunct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The four

kinds of chemical activity which it shows should therefore receive careful notice:

1. Water is a relatively stable substance.
2. It combines with many oxides, forming bases or acids.
3. It combines with many substances, chiefly salts, forming hydrates.
4. It interacts with some substances in a way described as hydrolysis. This property will not be discussed until a characteristic case is encountered.

Water a Stable Compound: Dissociation. In the case of a *compound*, the first chemical property to be given is always, whether the substance is relatively **stable** or **unstable**. Usually the specification is in terms of the temperature required to produce noticeable decomposition. Thus, potassium chlorate gives off oxygen at a low red heat. Now, water vapor, when heated, is progressively decomposed into hydrogen and oxygen, yet at 2000° the decomposition reaches only 1.8 per cent, and reunion occurs gradually as the temperature is lowered.

A decomposition which thus proceeds at higher temperatures, while at lower temperatures combination of the constituents can take place, is called a **dissociation**. The decomposition of potassium chlorate (p. 47) is not a dissociation because it is not reversible; oxygen will not under any circumstances reunite with potassium chloride.

Union of Water with Oxides. — When sodium combines with oxygen under certain conditions we obtain sodium oxide (Na_2O). The product unites violently with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2NaOH.$$

The slaking of quicklime is a more familiar action of the same kind:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

No other products are formed. The clouds of steam produced in the second instance are due to evaporation of a part of the water by the heat produced in the formation of calcium hydroxide. The aqueous solutions of these two products have a soapy feeling, and turn red litmus blue, and the substances therefore belong to the class of alkalies (pp. 66, 51) or **bases**. Very many hydroxides which are of

the same nature, for example ferric hydroxide $Fe(OH)_3$ and tin hydroxide $Sn(OH)_2$, are formed so slowly by direct union of the oxide and water that they are always prepared in other ways.

Some oxides, although they unite with water, give products of an entirely different character. Phosphoric anhydride and sulphur dioxide are of this class and, as we have seen (p. 51), yield acids.

These two classes of final products are so different that we make the distinction the basis for classification of the elements present in the original oxides. The elements, like sodium and iron, whose oxides give bases, are called **metallic elements**; those, like phosphorus, whose oxides give acids, are called **non-metallic elements**. The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead.

Hydrates. — Many substances when dissolved in water and recovered by spontaneous evaporation of the solvent enter into combination with the liquid. The products, which are solids, are called **hydrates**. That they are regular chemical compounds is shown by the following three facts: (1) These compounds show definite chemical composition expressible by formulæ in terms of chemical unit weights of the constituents. (2) Often much heat is given out in their formation. Thus, in the case of washing soda, the decahydrate of sodium carbonate (Na_2CO_3, $10H_2O$), the heat of the union (p. 55) is 8800 cal. (3) The hydrates have physical properties entirely different from those of their components. Thus, cupric sulphate, often called anhydrous cupric sulphate to distinguish it from the compound with water, is a white substance crystallizing in shining, colorless, needle-like prisms. The pentahydrate (blue-stone or blue vitriol), which crystallizes from the aqueous solution, is blue in color, and forms larger but much less symmetrical (asymmetric or triclinic) crystals (Fig. 26):

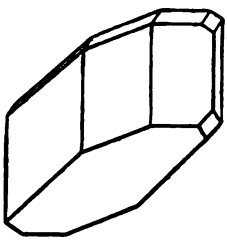

FIG. 26.

$$CuSO_4 + 5H_2O \rightleftarrows CuSO_4, 5H_2O.$$

The **chemical properties** show hydrates to be relatively unstable. When heated, the hydrates, as a rule, lose none of the constituents of

the original compound, but only the water, in the form of vapor. When melted, or when dissolved in water, the hydrates are dissociated (p. 81) into water and the original substance. The aqueous solutions made from the anhydrous substances and from the hydrates have identical physical and chemical properties. Hence the cheaper of the two forms is generally purchased, and many of the chemicals used in the laboratory are in the form of hydrates. In consequence of the ease with which hydrates give up water we write their formulæ (*e.g.* $CuSO_4$, $5H_2O$) so that the water and original substance are separate. A formula thus modified, so as to show some favorite mode of behavior of the substance, is called a **reaction** (p. 11) **formula.** The formula $H_{10}CuSO_9$, which would be equally correct, is never employed, because its use would disguise the relation of the substance to cupric sulphate.

The less stable hydrates dissociate very readily. Thus the decahydrate of sodium sulphate, $Na_2SO_4,10H_2O$ (Glauber's salt), loses all the water it contains (**effloresces**) when simply kept in an open vessel. When kept in a *closed* bottle, a very little of it loses water, and then the decomposition ceases. The cause of this we discover when a crystal of the hydrate is placed above mercury, like the ice or water in Fig. 25 (p. 79). *It shows a definite aqueous tension.* At 9° the value of this is 5.5 mm. As its temperature is raised, the tension increases. When the temperature is lowered, on the other hand, the tension diminishes, the mercury rises, and a part of the water enters into combination again. Different hydrates show different aqueous tensions at the same temperature. For example, at 30°, that of water itself is 31.5 mm., strontium chloride ($SrCl_2$, $6H_2O$) 11.5 mm., cupric sulphate ($CuSO_4$, $5H_2O$) 12.5 mm., barium chloride ($BaCl_2$, $2H_2O$) 4 mm.

In view of these facts, we perceive that loss of water by efflorescence is like evaporation. Those hydrates which, like Glauber's salt and washing soda, have a vapor tension approaching that of water itself, lose their water at ordinary temperatures at a rapid pace. Now, atmospheric air is usually less than two-thirds saturated with water vapor, and the partial pressure (p. 60) of this vapor *opposes the dissociation* and tends to prevent the liberation of the water. Thus at 9°, the vapor tension of water being 8.6 mm., the average vapor pressure of water in the atmosphere will be about 5 mm. Any hydrate with a greater aqueous tension than 5 mm.,

at 9°, such as Glauber's salt, will therefore decompose spontaneously in an open vessel. But those with a lower vapor tension, such as the pentahydrate of cupric sulphate with a tension of 2 mm. at 9°, will not do so (see pp. 90–93).

The water of hydration is known colloquially in chemistry as **water of crystallization.** The term was introduced when it was first observed that a hydrate, in decomposing, crumbles and loses its original crystalline form. But the term is misleading. All pure chemical substances, in solid form, when in stable physical condition, are crystalline. Amorphous (*i.e.*, non-crystalline) substances, like wax and glass, are supercooled liquids.

Composition of Water. — The proportion of hydrogen to oxygen, in water, by weight, is 2 : 15.879 or 2.015 : 16. The proportion by volume is 2.0027 volumes of hydrogen to 1 volume of oxygen. That the proportion by volume is very close to 2 : 1 may easily be shown by mixing hydrogen and oxygen in this proportion, in a strong tube, and exploding the mixture by means of a spark from an induction coil. The resulting steam condenses and the whole gas vanishes. If different proportions are used, the excess of one of the gases remains uncombined.

Gay-Lussac's Law of Combining Volumes. — The almost mathematical exactness with which small integers express this proportion is not a mere coincidence. **Whenever gases unite, or gaseous products are formed, the proportions by volume** (measured at the same temperature and pressure) **of all the gaseous bodies concerned can be represented very accurately by ratios of small integers.** This is called **Gay-Lussac's law of combining volumes** (1808). Thus, when the above experiment is carried out at 100°, in order that the product, water, may be gaseous also, it is found that the three volumes of the constituents give almost exactly two volumes of steam. For example, 15 c.c. of hydrogen and 7.5 c.c. of oxygen give 15 c.c. of steam. Of course the hydrogen, oxygen, and steam must be measured at the same pressure, and the temperature must remain constant (100°) during the experiment. Proper manipulation secures the former, and a jacket filled with steam (Fig. 27) the latter condition. Strips of paper, 1, 2, and 3, are pasted on the jacket in such a way that equal lengths of the eudiometer, in this case a straight one, are laid off. The three divisions being filled with a mixture of hydrogen

and oxygen in the proper proportions, the gas, after the explosion, shrinks so as to occupy, at the same pressure, only two of them.

From this universal truth in regard to the combination of gases, we draw the important inference that **the chemical unit-weights of simple substances,** and the formula-weights of compounds, **in the gaseous condition, occupy at the same temperature and pressure volumes which are equal, or else stand to one another in the ratio of small integers.**

FIG. 27.

Exercises. — 1. Name some familiar transitions (p. 78) from one physical state to another.

2. What evidence is there in the common behavior of ether and chloroform to show that these liquids have high vapor tensions?

3. If the pressure of the steam in a boiler is ten atmospheres, at what temperature is the water boiling (p. 80)?

4. How many grams of water could be heated from 20° to 100° by the heat required to melt 1 kgm. of ice at 0°?

5. What do you infer from the fact that alum and washing soda lose their water of hydration when left in open vessels, while gypsum does not?

6. Which fact shows most conclusively that hydrates are true chemical compounds?

7. Gypsum is a hydrate of calcium sulphate ($CaSO_4$). If 6 g. of gypsum, when heated, lose 1.256 g. of water, what is the formula of the hydrate?

8. In what ways does a hydrate differ from, (*a*) a solution, (*b*) an hydroxide?

9. Should you expect to find any difference, in respect to chemical activity, between the three forms of water? Have we had any experimental confirmation, or the reverse, of this conclusion (p. 66)?

10. Name some crystalline substances which are not used, or do not occur in the form of hydrates.

CHAPTER IX

THE KINETIC-MOLECULAR HYPOTHESIS

As soon as we have constructed a law (p. 4) we desire immediately to find out the basis of the constant mode of behavior it epitomizes. If no explanation, that is, more detailed description, is forthcoming as the result of closer observation, we proceed to *imagine* one (p. 5). This always takes a mechanical form, often crude at first, and later undergoing refinement. Thus, at first, the phenomena of light were explained by the conception of clouds of fine corpuscles emanating from the luminous body. The chances of hitting upon an objective reality by guess-work like this is obviously remote. Whether such particles did really fly about was not the main question, however. Their value lay in the fact that they could be pictured concretely and gave a basis for further thought and perhaps suggestions for new experiments. Such a structure of the imagination is called an **hypothesis**.

The Molecular Hypothesis. — The only mechanical basis we can imagine to account for the physical properties of matter is a discontinuous structure of some description. The fact that all kinds of matter can be compressed (gases to an enormous extent, solids and liquids to a measurable extent) may be explained, either by a diminution in the volume of the material itself, or by the closer packing together of the particles into which this material is divided. It is evident that the latter is much more in harmony with our experience. Oxygen at 760 mm., for example, can be reduced by pressure to one two-hundredth of its volume, or even less. Compression, we imagine, therefore, does not here diminish the actual volume occupied by oxygen, but crowds the particles closer together and diminishes to one two-hundredth the space between them. Compressing a gas is, in fact, mainly compressing the *empty space* of which we imagine it chiefly to consist. The same hypothesis will furnish a concrete description of how one kind of matter will frequently absorb a large

quantity of another. Thus we picture the hydrogen gas taken up by iron and other metals as being packed away in the spaces between the particles of the metal. So also, in solution, the volume of the liquid does not usually increase by an amount equal to that of the substances dissolved. Hence we imagine the particles as possibly incompressible and the interstices between them as furnishing a part of the accommodation for the foreign material. A *particle* is a fragment of matter which can be seen and measured directly, and handled separately. Since the particles of this hypothesis have none of these qualities, we distinguish them by the name **molecules. Molecules are the imaginary units of which bodies are aggregates.**

In the following sections the term *particle*, when used at all, is usually equivalent to *molecule*, and is employed only to avoid too frequent occurrence of the latter word.

Kinetic-Molecular Hypothesis Applied to Gases. — Let us first build up our hypothesis to fit the *qualitative* properties of gases. We print in italics each *fact*, and in black type the part of the **hypothesis** invented to fit it. The most remarkable thing about a gas, considering the looseness with which its material is packed, is the total *absence* in it of any tendency to *settling* or subsidence. Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to suppose that they are **widely separated from one another,** and that they occupy the space, otherwise a complete vacuum, by **constantly moving about in all directions.** But a moving aggregate of particles which does not even finally settle must be in perpetual motion. We must, therefore, imagine the molecules to be wholly unlike particles of matter in having **perfect elasticity,** in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The *diffusibility* of gases and their mutual *permeability* require no additional assumptions. The fact that each gas is *homogeneous*, efforts to sift out lighter or heavier samples having failed, requires the supposition that **all the molecules** of a pure gas are **closely alike.**

Passing now to *Boyle's law* (p. 59), the thing to be accounted for is that when a sample of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 28) represent a cylinder with a movable piston, upon which weights may be

placed to resist the pressure. Now the pressure exercised by the gas under the piston cannot be like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon the piston produce. If this is the case, the compressing of a gas must consist simply in moving the partition downwards so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter. Their impacts upon the wall become more and more frequent. So the pressure which this causes becomes greater and greater, and is proportional to the degree of crowding (concentration) of the molecules. There are two other points to be added. When we diminish the volume to one-half, we find from experience that the pressure becomes exactly, or almost exactly, twice as great. This must mean that although the particles are becoming crowded they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of molecules per unit of volume give exactly double the number of impacts on the walls. Hence the molecules must have practically no tendency to cohesion. Finally, the molecules must be supposed to move in straight lines between collisions.

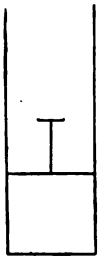

FIG. 28.

Boyle's law therefore adds four more conceptions to our molecular hypothesis, namely, that the **impacts of the particles** produce the *pressure*, that the **crowding of the molecules** represents the *concentration of the material* and that the particles **move in straight lines** and **show almost no cohesion**, since *pressure* and *concentration are very closely proportional to one another.*

How, now, can we account for *Charles' law* (p. 60), according to which an increase in pressure (or in volume) results from heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity. It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore **increase the velocity of each** since the kinetic energy of all becomes greater.

The fact that the *combining volumes of gaseous substances are equal, or stand to one another in the ratio of small whole numbers* (Gay-Lussac's law, pp. 84–85), suggests two ideas: First, that chemical combination, considered in detail, and arranged to harmonize with this hypothesis, would involve **unions of** a few **particles** of more than one kind to form **composite molecules.*** And, second, that a simple integral relation must be assumed to exist between the **numbers of molecules in equal volumes of different gases,** at the same temperature and pressure. Avogadro (1811), the professor of physics in Turin, put forward the hypothesis that these numbers **might be equal.** A more strict study of the assumptions we have been making, and of some additional facts, has since shown that no other conjecture than Avogadro's would be consistent with them. Thus it now bears the relation of a logical deduction from the kinetic-molecular hypothesis and the properties of gases, and is known as **Avogadro's hypothesis.** It may also be put in the form: **At the same temperature and pressure, the molecular concentration of all kinds of gases has the same value.**

The *law of diffusion* (p. 74) harmonizes with the kinetic-molecular hypothesis without further modification of the latter.

Finally, gases can be *liquefied by sufficient cooling and compression.* This fact compels us to suppose that, after all, even gaseous molecules have a tendency to **cohesion.** This cohesion is scarcely perceptible so long as the gas is warm and diffuse. But when the kinetic energy of the molecules is sufficiently reduced by cooling (namely, to the *critical temperature*), and the molecules are brought sufficiently close together, the mutual cohesion of the molecules causes the gas to condense and assume the liquid form. The critical temperature of oxygen is $-118°$, of hydrogen $-234°$, of carbon dioxide 31.35°, of water 358°.

We may summarize the facts about gases, appearing in italics above, with the corresponding fictions, in heavy type, which we have added one by one in manufacturing our hypothesis, as follows:

* This is essentially the idea used by Dalton, before Gay-Lussac's law was known, however, for the explanation of the laws of chemical combination. He called it the atomic hypothesis (*q.v.*).

Facts.	Hypothesis.
Non-settling Compressibility Diffusibility Permeability	The fictitious particles called molecules are, at 0° and 760 mm., at great average distances from one another; they are in constant motion and have perfect elasticity.
Homogeneity.	The molecules of the same substance are closely alike.
Relation of pressure and concentration (Boyle's law).	The effect of pressure is produced by the impacts of the molecules, and is proportional to the degree to which they are crowded together; the molecules move in straight lines, and, when widely scattered, exhibit almost no tendency to cohesion.
Relation of volume (or pressure) and temperature (Charles' law).	A rise in temperature increases the velocity and therefore the kinetic energy of the molecules.
Relation of atomic weights and volumes (Gay-Lussac's law). Law of diffusion.	Chemical union consists in fusion of different kinds of molecules (Dalton's hypothesis), of which there are equal numbers in equal volumes of different gases at the same temperature and pressure (Avogadro's hypothesis).
Gases can be liquefied.	Molecules do possess a tendency to cohesion, which they exhibit when cooled and closely crowded together.

Kinetic Hypothesis Applied to Liquids.—The phenomena connected with surface tension, such as coherence into drops, show that cohesion plays a larger part in liquids than in gases. On the other hand, liquids which are capable of mixing (*e.g.* alcohol and water), when placed above one another in the same vessel, do mix, slowly, by diffusion. This indicates that motion of the molecules, although much impeded by friction, has not been annihilated by cohesion.

The formation of vapor from cold liquids likewise requires us to make the same supposition. To be consistent, we have also to imagine that the vapor above the liquid, for example the water in the barometer tube in Fig. 25 (p. 79), is not composed of the same

set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the liquid, while others emerge and take their places. When the water is first introduced, there are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes greater, hence the mercury column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. The rate at which molecules return to the water thus begins at zero, and increases steadily: the rate at which molecules leave the water maintains a constant value. Hence the rate at which vapor molecules enter the water must eventually equal that at which other molecules leave the liquid. At this point, occasion for visible change ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest but of rapid and equal exchange. Such, described in terms of the hypothesis, is the state of affairs which is characteristic of a condition of **equilibrium**. The condition is kinetic, and not static.

Equilibrium. — This term is used so often in chemistry, and is used in so unfamiliar a sense, that the reader should consider attentively what it implies. Three things are characteristic of a state of equilibrium:

1. There are always *two opposing tendencies* which, when equilibrium is reached, balance one another. In the foregoing instance, one of these is the hail of molecules leaving the liquid, which is constant throughout the experiment. It represents the **vapor tension of the liquid** (p. 79). The other is the hail of returning molecules, which, at first, increases steadily as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor.** These have the effect of opposing pressures, and, when the latter becomes equal to the former, *equilibrium* is established. In all cases of equilibrium we shall symbolize the two opposing tendencies by arrows, thus:

$$\text{Water (liq.)} \rightleftarrows \text{Water (vapor)}.$$

2. Although their effects thus neutralize one another at equilibrium, both tendencies *are still in full operation.* In the case in point,

the opposing hails of molecules are still at work, but neither can effect any visible change in the system. Equilibrium is a state of balance or poise, not of rest.

3 (and this is the chief mark of equilibrium). A slight change in the conditions produces, never a great or sharp change, but always, and instantly, a *corresponding small change* in the state of the system. The change in the conditions accomplishes this by *favoring or disfavoring one of the two opposing tendencies.* Thus, for example, when the temperature of a liquid is raised, the kinetic energy of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases and, hence, a greater concentration of vapor can be maintained. The system, therefore, quickly reaches a new state of equilibrium in which a higher vapor pressure exists (p. 79). A heap of matter on a table is not in equilibrium, because addition of more material produces no response until, when a very great quantity is added, the table breaks. But a body on the scales is in equilibrium, for the addition of the smallest particle produces a corresponding inclination of the beam.

In the preceding illustration, the evaporating tendency was favored by a rise in temperature. As an example of a change in conditions *disfavoring* one tendency, take the case where the liquid is placed in an *open*, shallow vessel. Here the condensing tendency is markedly discouraged, for there is practically no return of the emitted molecules. Hence complete evaporation takes place. Elevation of the temperature hastens the process. A draft insures the total prevention of all returns, and has therefore the same effect. The two methods of assisting the displacement of an equilibrium, and particularly the second, in which the opposed process is weakened and the forward process triumphs solely on this account, should be noted carefully. They are applied with surprising effectiveness in the explanation of chemical phenomena (see Chaps. xi and xv).

Kinetic Hypothesis Applied to Solids. — The properties of solids differ from those of liquids chiefly in the fact that the solid has a definite form of which it can be deprived only with difficulty. This we may explain in accordance with the kinetic hypothesis by the supposition that the cohesion in solids is very much more prominent than in liquids. We obtain solids from liquids by cooling them; in other words, by diminishing the kinetic energy and therefore the

velocity of the particles. The cohesive tendency of the latter is thus able to make itself felt to a greater extent. If, conversely, we heat a solid, or, according to the hypothesis, if we increase the speed with which the particles move, the body first melts and gives a liquid, and this finally boils and becomes a gas. The intrinsic cohesion of the particular substance can undergo no change, but the increasing kinetic energy of the particles steadily and continuously obliterates its effects. Yet some motion still survives in a solid. Thus we find that when the layer of silver is stripped from a very old piece of electroplate, the presence of this metal in the German silver or copper basis of the article is easily demonstrated.

The tendency of all solids to assume crystalline forms, which show definite cleavage and other evidences of **structure**, distinguishes them sharply from liquids. The force of cohesion in liquids is exercised equally in different directions. In solids it must differ in different directions in order that structure may result. Since each substance shows an individual structure of its own, these directive forces must have special values in magnitude and direction in each substance.

A crystal arises by growth. When the process is watched, as it occurs in a melted solid or an evaporating solution, the slow and systematic addition of the material in lines and layers, as if according to a regular design, is one of the most beautiful and interesting of natural phenomena. The fern-like patterns produced by ice on a window-pane show the general appearance characteristic of crystallization in a thin layer. A larger mass in a deep vessel gives forms which are geometrically more perfect. From its very incipiency the crystal has the same form as when, later, its outlines can be distinguished by the eye. Hence the outward form is only an expression of a specific internal structure which the continual reproduction of the same outward form on a larger and larger scale leaves as a memorial of itself in the interior.

Crystal Forms. — Crystalline form is continually used in identifying (pp. 6, 9, 24–25) the substances produced in chemical actions. The classification of crystalline forms is carried out according to the degree of symmetry of the crystals:

1. Regular system.
2. Square prismatic system.
3. Hexagonal system.
4. Rhombic system.
5. Monosymmetric, or monoclinic system.
6. Asymmetric, or triclinic system.

The **regular system** presents the most symmetrical figures of all. Some forms which commonly occur are the octahedron (Fig. 29) shown by alum, the cube (Fig. 6, p. 8) affected by common salt, and the dodecahedron (Fig. 30) frequently assumed by the garnet.

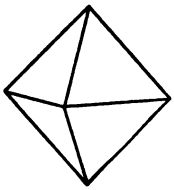

FIG. 29.

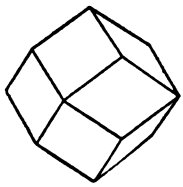

FIG. 30.

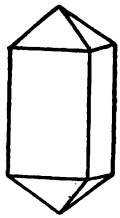

FIG. 31.

The **square prismatic system** includes less symmetrical forms than the previous one, since the crystals are lengthened in one direction. Fig. 31 shows the condition in which zircon ($ZrSiO_4$), which furnishes us with the basis of certain incandescent illuminating arrangements, occurs in nature. The form of ordinary hydrated nickel sulphate ($NiSO_4$, $6H_2O$) is similar to this.

The **hexagonal system**, like the preceding, frequently exhibits elongated prismatic forms,

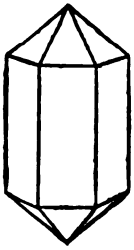

FIG. 32.

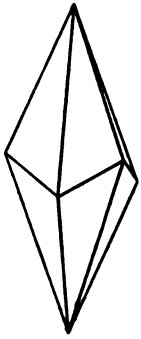

FIG. 33.

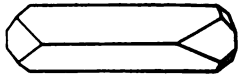

FIG. 34.

but the section of the crystals is a hexagon, instead of a square, and the termination is a six-sided pyramid. Quartz (Fig. 32), or rock crystal, is the most familiar mineral in this system. Calcite ($CaCO_3$), which is chemically identical with chalk, or marble, takes forms known as the scalenohedron (Fig. 33) and rhombohedron (Fig. 9, p. 9), which are classified in a subdivision of this system. Indeed, recently it has become common to erect this into a

separate system (the trigonal), in which both quartz and calcite are included.

The **rhombic system** includes the natural forms of the topaz, and of sulphur (Fig. 1, p. 6), as well as that of potassium permanganate (Fig. 34), potassium nitrate (Fig. 63), and many other substances. These crystals exhibit a good deal of symmetry, but their section is always rhombic, and hence the name.

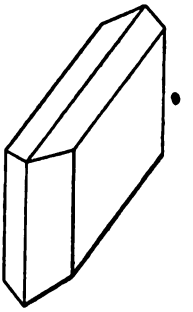

FIG. 35.

The **monosymmetric system** exhibits forms which have but one plane of symmetry. Gypsum (Fig. 35), which is hydrated calcium sulphate ($CaSO_4$, $2H_2O$), and felspar are minerals possessing forms of this kind. Tartaric acid, rock candy (Fig. 36), potassium chlorate, and hydrated sodium carbonate (washing soda) belong to this system.

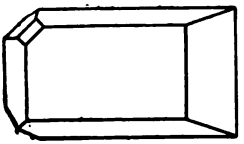

FIG. 36.

The **asymmetric system** includes forms which have no plane of symmetry whatever. Blue vitriol (Fig. 26, p. 82), $CuSO_4$, $5H_2O$, is one of the most familiar substances of this kind.

CHAPTER X

SOLUTION

SOLUTIONS are so constantly used in chemistry that some knowledge of their properties is desirable in order that we may employ them intelligently. In what follows, we give a preliminary account of some of the simpler facts about solution.

General Properties of Solutions. — A solid may be distributed through a liquid, either by being simply suspended (p. 77) in the latter (mixture), or by being dissolved in it (solution). Similarly a liquid may be suspended in droplets in another (emulsion), as in milk, or it may be dissolved. It is usually easy to distinguish between the two cases, for a suspended substance *settles* or separates sooner or later, while a dissolved one shows *no such tendency*. The cases are exceptional where the subdivision of a suspended substance is so minute (colloidal solution) as to make its retention by filter paper impossible. If a liquid is opalescent or opaque, then we have a case of suspension. A solution is a clear, transparent, perfectly homogeneous liquid, in which the dissolved substance seems to have been dispersed so completely that the liquid cannot be distinguished by the eye from a pure substance.

There is no limit to the amount of dissipation which may thus be produced. A single fragment of potassium permanganate, for example, which gives a very deep purple solution in water, may be dissolved in a liter or even in twenty liters of water, and the purple tinge which it gives to the liquid will still be perfectly perceptible in every part of the larger volume. **The qualitative characteristics,** therefore, **of solution** are **absence of settling, homogeneity, and extremely minute subdivision of the dissolved substance.**

The Scope of the Word. — The word is used for other systems than those containing a solid body dissolved in a liquid. Thus, liquids also may be dissolved in liquids, as alcohol in water. Again,

if we warm ordinary water, bubbles of gas appear on the sides of the vessel before the water has approached the boiling-point. They are found to be gas derived from the air. Agitation of any gas with water results in the solution of a large or small quantity of the gas, and heat will usually drive the gas out again. It appears therefore that solids, liquids, and gases can equally form solutions in liquids.

The absorption of hydrogen by palladium (at all events after a certain point), and by iron, takes place in accordance with the same laws as the solution of solids in liquids, and the results may be described therefore as true solutions. Liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are perfectly familiar. The sapphire is a solution of a small amount of a strongly colored substance, in a large amount of colorless aluminium oxide. It may therefore be stated that solution of gases, liquids, and solids in solids appears to be possible.

Limits of Solubility. — The next question which naturally occurs to us is as to whether the mingling of two substances in this manner has any limits. We find that the results of experiment in this direction may be divided into two classes. Some pairs, of liquids particularly, may be mixed in any proportions whatever. Alcohol and water is such a pair. On the other hand, at the ordinary laboratory temperature, we can scarcely take a fragment of marble ($CaCO_3$) so small that it will dissolve completely in 100 c.c. of pure water. Under the same conditions any amount of potassium chlorate up to 5 g. will almost completely disappear after vigorous stirring, while 90 g. of ordinary Epsom salts (hydrated magnesium sulphate), but not more, may be dissolved in about the same amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which with different solids may range from a scarcely perceptible to a very large amount. No substance is absolutely insoluble. But for the sake of brevity we call marble, for example, " insoluble " because in most connections it may be so considered.

Recognition and Measurement of Solubility. — The only method of recognizing with certainty whether a solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning how much of the body is contained in a given solution, a weighed quantity of the

solution is evaporated to dryness and the weight of the residue determined.

It must be stated explicitly that in going into *solution*, as we have used the term, a compound dissolves as a whole and, if the compound is pure (p. 23), any residue has the same chemical composition as the part which has dissolved.

Terminology. — In order to describe the relations of the components of a solution, certain conceptions and corresponding technical expressions are required. It is customary to speak of the substance which, like water in most cases, forms the bulk of the solution, as the **solvent**. To express the substance which is dissolved, the word **solute** is frequently used, and will be employed when we wish to avoid circumlocution. The amount of the substance which has been dissolved by a given quantity of the solvent is described as the **concentration** of the solution. A solution containing a small proportion of the dissolved body is called **dilute**; it has a small concentration. One which contains a larger amount is **more concentrated**. Very "strong" solutions are frequently spoken of simply as **concentrated solutions**. The *partial* removal of the solvent (as by evaporation) is called **concentrating**, its total removal **evaporating to dryness**. Finally, since there is a limit to the solubility of most substances, a solution is described as **saturated** when the solute has given as much material to the solvent as it can. This state is reached after prolonged agitation with *an excess* of the gas, of the liquid, or of the *finely powdered* solid, as the case may be (see pp. 102, 107). Other things being equal, the larger the excess, the sooner saturation is attained. The maximum concentration attainable in this way is called the **solubility** of the substance in a given solvent.

The concentrations of solutions, saturated and otherwise, are sometimes expressed in physical, and sometimes in chemical, units of weight. When physical units are employed, we give the number of grams of the solute held in solution by one hundred of the solvent.

When chemical units of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 32) or the atomic weights may be taken as a basis of measurement. In the former case, the solutions are called **normal solutions**, and in the latter, for a reason which will appear later (Chap. xii), **molar solutions**.

A normal solution contains one gram-equivalent of the solute in one liter of solution. The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. **An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element.** Thus, a formula-weight of hydrochloric acid HCl (36.5 g.) is also an equivalent weight, for it contains 1 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H_2SO_4 (98 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride $AlCl_3$ (133.5 g.) three equivalents. Hence normal solutions of these three substances contain respectively 36.5 g. (HCl), 49 g. (H_2SO_4), and 44.5 g. ($AlCl_3$) per liter of solution. The special property of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis. We frequently use also decinormal or one-tenth normal solutions ($.1\ N$ or $N/10$), and seminormal ($.5\ N$ or $N/2$), and six times normal solutions ($6\ N$), and so forth.

A molar solution contains one mole (gram-molecular weight) of the solute in one liter of solution. When molecular formulæ (see Chap. xii) are used, this means one gram-formula weight per liter. In the cases cited above, the molar solution contains 36.5 g. (HCl), 98 g. (H_2SO_4), and 133.5 g. ($AlCl_3$) per liter. As will be seen, the concentrations of molar and normal solutions are necessarily identical when the radicals are univalent.

The **solubilities** at 18° of **one hundred and forty-two bases and salts** are given in a **table** printed **inside the cover, at the front of this book.**

Solution One of the Physical States of Aggregation of Matter. — When a solid body dissolves in a liquid, the properties of the body undergo a very marked change, which to all appearance might be chemical. Yet, besides the ease with which a liquid may be removed by evaporation and the solid recovered unchanged, we note particularly that the concentration of a saturated solution cannot be expressed in terms of integral multiples of the chemical combining weights. We shall see also that the quantity of a solid which a liquid may take up varies with the slightest change in temperature. Now we do not find the composition of chemical compounds so to

vary. The solution of a solid may therefore be likened to a change in state of aggregation, similar to the conversion of a liquid into a gas or a solid.

As in other changes of state, so in the process of solution, heat is always liberated or absorbed. This is known as **heat of solution.** Thus, one formula-weight of sulphuric acid, in dissolving in a large volume of water, liberates 39,170 calories, and one formula-weight of ammonium chloride, in dissolving, absorbs 3880 calories.

As there is danger of confusion arising, we may repeat that a compound is homogeneous and its composition is expressible in chemical units of weight; a saturated solution is homogeneous but its concentration varies with temperature so that chemical units cannot be used to describe its composition; a mixture of two solids, or an emulsion of two liquids, is neither homogeneous nor in any way definite in composition.

Kinetic-Molecular Hypothesis Applied to the State of Solution. — Accepting solution as a physical state of aggregation, we may now apply the same formulative hypothesis to the explanation of the behavior of a substance in solution as to matter in the gaseous or liquid states. We saw that a solid body, which is ordinarily condensed in a small space, can be disseminated by the use of a solvent through a very large one. The molecules of the solid become scattered like those of a gas or vapor through a much greater volume. We may regard the dissolved substance as being, practically, in a gaseous or *quasi*-gaseous condition. The molecules are torn apart from one another, their cohesion is overcome, and their freedom of motion is in a measure restored. It is true that they could not continue to occupy this large volume for a moment in the absence of the solvent. But we may bring this into relation with the case of a vapor by saying that a solid body, like common salt, can only evaporate (*i.e.* "dissolve") at the ordinary temperature, and occupy a large space, when that space is already filled with a suitable liquid. The latter acts as a vehicle for the particles of the solid. A volatile liquid, on the contrary, can dissolve in an *empty* space and fill it with its particles without any vehicle being required.

This conception of the *quasi*-gaseous condition of a dissolved substance would be simply fantastic if it did not lead us to a better understanding of the behavior of solutions. It does successfully

explain many things, such as diffusion, osmotic pressure, and saturation (see next section).

It is easy to show that, if we place a quantity of the pure solvent (Fig. 37) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig. 38), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the particles of the dissolved

Fig. 37.

Fig. 38.

substance exhibit the property of diffusion in the same way as do those of gases.

When the diffusion of a *gas* is resisted by a suitable partition, we find pressure is exercised upon the walls of the vessel and upon the partition. It is possible to show that the particles of a *dissolved substance* exercise a pressure of a very similar kind. This pressure is spoken of as **osmotic pressure.** This pressure is found to be proportional to the concentration of the solution, just as gaseous pressure is proportional to the concentration of the gas (Boyle's law).

Kinetic-Molecular Hypothesis Applied to the Process of Solution. — We may now apply the same hypothesis to the process of dissolving, with a view more especially to explaining why the

process of dissolving ceases, in spite of the presence of excess of the solute, when a certain concentration has been reached. If some of the material dissolves, why not more?

Let us suppose that it is the dissolving of common salt in water (Fig. 39) which we wish to explain in detail. We believe that in the solid substance the molecules are somewhat closely packed together, while in the solution they are rather sparsely distributed. The process of solution must consist in the loosening of the molecules on the surface and their passage into the liquid. By diffusion, the free molecules will gradually move away from the neighborhood of the surface of the solid and make room for others, and thus, if the system remains undisturbed, the liquid will eventually become a solution of uniform concentration. If a large enough amount of the solid has been provided, the ultimate condition will be that of a saturated solution with excess of the solid beneath. If we had proper means of measuring it, the tendency of the molecules to leave the solid in the presence of a given liquid would give the effect of a kind of pressure. This is spoken of as **solution pressure.**

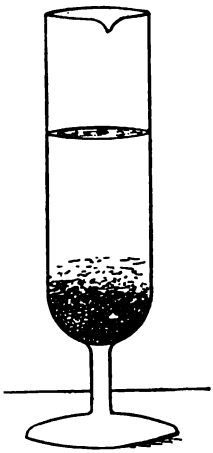

FIG. 39.

Now the molecules, after having entered the liquid, move in every direction, and consequently some of them will return to the solid and attach themselves to it. The frequency with which this will occur will be greater as the crowding of particles in the liquid increases, so that a stage will eventually be reached at which the number of molecules leaving the solid will be no greater than that landing upon it in a given time. If the whole of the liquid has meanwhile become equally charged with dissolved molecules, there will be no chance that the field of liquid immediately round the solid will lose them by diffusion, so that a condition of balance or equilibrium (p. 91) will have been established: NaCl (solid) $\rightleftarrows$ NaCl (dslvd). The motion of the particles in the liquid produces what we have called osmotic pressure; and *when the osmotic pressure,* by the continual increase in the number of dissolved molecules, *becomes equal to the solution pressure,* increase in concentration of the solution

ceases. It is at this point that *we speak of the solution as being saturated* with respect to the particular substance dissolving. The analogy to vapor tension and vapor pressure (p. 79) is evident. The foregoing explanation should be compared carefully with that given in the section on the kinetic hypothesis applied to liquids, and in that on equilibrium (pp. 90–93).

When the dissolving substance is a **gas**, led through, or confined above the liquid at a definite pressure, the gas dissolves until a state of equilibrium between dissolving and emission is reached, for example, Oxygen (gas) $\rightleftarrows$ Oxygen (dslvd), and the liquid is then saturated with the gas.

It is found, as the hypothesis would lead us to expect, that **the concentration of the saturated solution of a gas is proportional to the pressure at which the gas is supplied (Henry's law).**

Independent Solubility. — Just as two gases, when mixed, are independent of one another (p. 60), and have severally the same pressure, solubility, and so forth, as they would possess if each alone occupied the same space, so is it with dissolved substances. In general, a volume of water, in which a moderate amount of some substance has been dissolved, will take up as much of a second substance as would an equal volume of pure water. Thus, water containing some sugar will dissolve as much sodium chloride as the same amount of pure water. In the point of view of the kinetic-molecular hypothesis, the dissolved molecules of sugar have no connection with, or influence upon, the mechanism which determines the solubility of the salt, namely, the exchange of salt molecules between the suspended, dissolving crystals and the solution.

Two Immiscible Solvents: Law of Partition.—An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. If now ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance partially from solution in one solvent and securing it in another is called **extraction.** We find in such cases that neither sol-

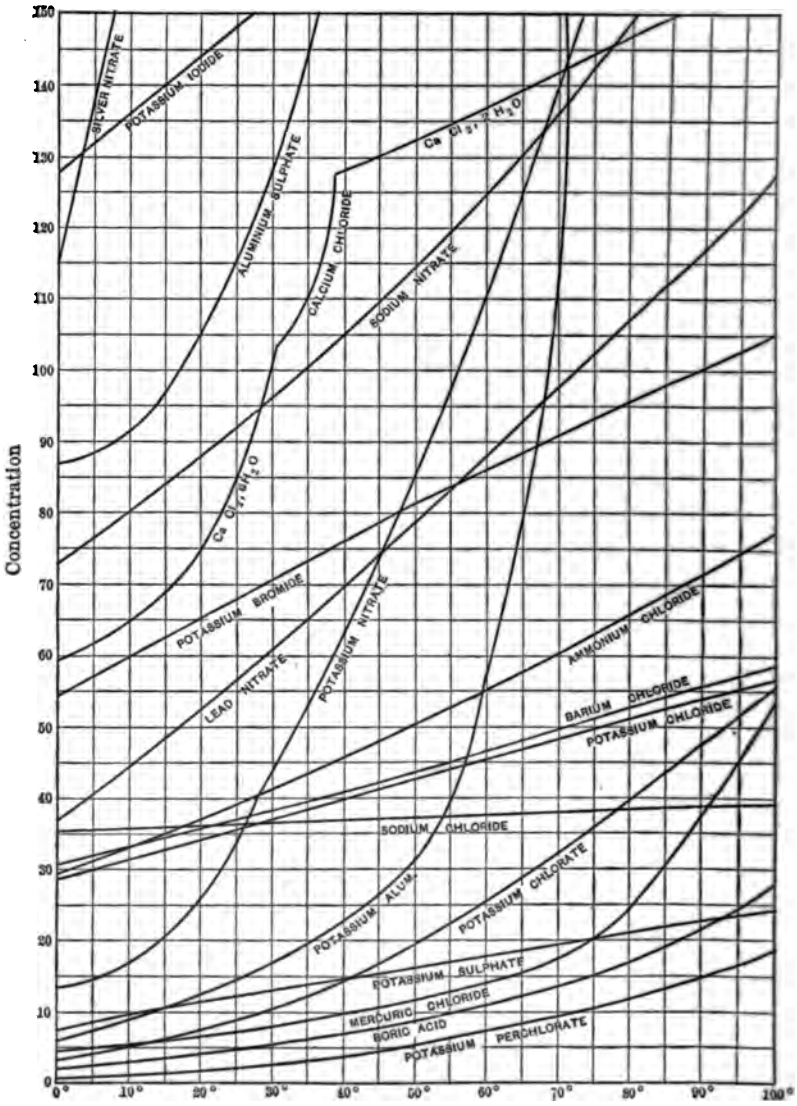
Concentration
Temperature
SILVER NITRATE
POTASSIUM IODIDE
ALUMINIUM SULPHATE
CALCIUM CHLORIDE
Ca Cl2, 2 H2O
SODIUM NITRATE
Ca Cl2, 6 H2O
POTASSIUM BROMIDE
LEAD NITRATE
POTASSIUM NITRATE
AMMONIUM CHLORIDE
BARIUM CHLORIDE
POTASSIUM CHLORIDE
SODIUM CHLORIDE
POTASSIUM ALUM
POTASSIUM CHLORATE
POTASSIUM SULPHATE
MERCURIC CHLORIDE
BORIC ACID
POTASSIUM PERCHLORATE

FIG. 40.

vent can entirely deprive the other of the whole of the dissolved substance, if the latter is soluble in both independently. A state of equilibrium is finally reached: I (in Aq) $\rightleftarrows$ I (in ether). The partition of the substance takes place in proportion to its solubility in each solvent. It is found that any amount of the solute, up to the maximum the system can contain, provided this does not involve too high a concentration in either solvent, is divided so that the ratio of the concentrations in the two solvents is always the same. In the case of iodine divided between water and ether, this ratio is about 1 : 200.

Influence of Temperature on Solubility. — The quantity of a substance which we can dissolve in a fixed amount of a given solvent depends very largely upon the temperature of both. Usually the solubility increases with rise in temperature. Measurements may be made by the method described before (p. 97), using *excess* of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 40) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is held in solution by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus 100 g. of water holds 13 g. of potassium nitrate in solution at 0° and 150 g. at 73°. The increase in solubility is here enormous. On the other hand, the same quantity of water will hold 35.6 g. of sodium chloride in solution at 0° and 39 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility decreases with rise in temperature are less common. Anhydrous sodium sulphate (Fig. 41, p. 106) is an illustration.

Equilibrium in a Saturated Solution. — Once a solution has become saturated, the dissolving substance remains thereafter unchanged in *amount*. A greater excess of the solute forces no more matter into solution than does a small excess.

It should be clearly understood, however, that the kinetic hypothesis requires us to assume that an exchange of molecules (p. 102) is still going on between the solid and the solution. That this conception is correct may be shown in various ways. Thus, if a crystal, the edges or corners of which have been broken, is suspended in a saturated solution of the same substance, it neither increases nor diminishes in weight. Yet we find that the imperfections are removed, and that this takes place by the solution of a portion of the substance from the perfect surfaces and its deposition upon the imperfect ones.

Another very striking proof of this may be obtained by saturating water with ordinary Glauber's salt (hydrated sodium sulphate,

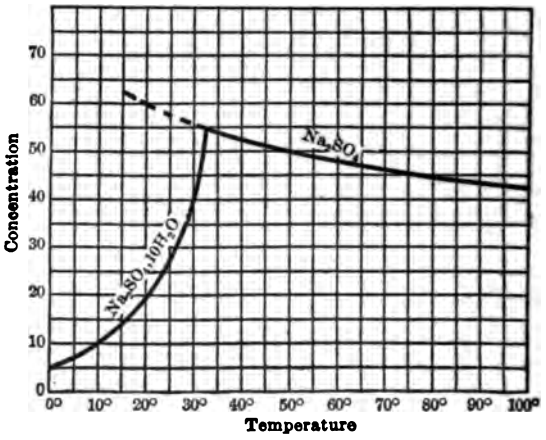

FIG. 41.

Na_2SO_4, $10H_2O$) at a temperature somewhat above the ordinary, say 30°. The excess of the solid is carefully and completely separated from the liquid, and the latter is allowed to cool in a flask loosely stoppered with cotton. The solution now contains (Fig. 41) a much larger amount of sodium sulphate (Na_2SO_4) than at its present temperature it could acquire from contact with Glauber's salt. Yet in the absence of a crystal, with which the above described exchange could take place, no deposition of the dissolved substance begins. The solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the deca-

hydrate at once starts the exchange, and this is necessarily very much to the disadvantage of the solution and the advantage of the crystal: Na_2SO_4 (dslvd) $\rightleftarrows$ $Na_2SO_4,10H_2O$ (solid). The latter therefore forms the center of a radiating mass of blade-like processes, which sprout with astonishing rapidity through the liquid.

Usually the cooling of a concentrated solution leads to the almost immediate appearance of crystals spontaneously, and the substance is deposited gradually as the temperature falls. But solutions of a number of common substances, such as sodium thiosulphate (photographer's " hypo ") and sodium chlorate, behave like that of sodium sulphate. They are said to have a tendency to give **supersaturated solutions.** In general, crystallization can be started only by introduction of a specimen of the same substance. The smallest particle of the right material floating in the air, if it gains admission, will bring about the result. This shows the importance of the interchange of molecules, of which we have spoken, for establishing equilibrium.

To avoid a common **misconception,** it must be noted that a saturated solution is *not* one containing all of the solute that it can hold. A supersaturated solution contains more. The **saturated solution** is one which contains all of the dissolved solute that it can acquire from the undissolved solute. Better still, it is **that solution which, when placed with excess of the solute, is found to be in equilibrium.**

Exercises. — 1. Give other examples of limited solubility in various solvents (p. 97).

2. What weights of phosphoric acid (p. 51) and of sodium hydroxide, respectively, are required to make 1 liter of a normal solution?

3. Express the concentrations of solutions of ammonium chloride, saturated at 0° (sp. gr. 1.076), and of potassium sulphate K_2SO_4, saturated at 10° (sp. gr. 1.083), in terms of a normal solution (p. 99).

4. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

5. Explain why, (*a*) pulverization and, (*b*) agitation hasten the dissolving of a solid?

6. Read from the curves (p. 104) the solubilities of potassium nitrate at 15°, of potassium chloride at 30°, of potassium chlorate at 45°. What are the relative rates at which the solubilities of these salts increase with rise in temperature?

CHAPTER XI

CHLORINE AND HYDROGEN CHLORIDE

CHLORINE was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the method described below.

Occurrence. — Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Of the 3.6 per cent of solid matter in sea-water, nearly 2.8 is common salt (sodium chloride, NaCl). During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride, called by the mineralogist halite (rock salt). In other layers potassium chloride (sylvite), and hydrated magnesium chloride (bischofite), and other compounds of chlorine, occur. The chloride of silver (horn silver) is a valuable ore.

Preparation. — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen (*cf.* p. 67). We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (p. 64). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride (HCl), and by means of some simple substance which is capable of uniting with the other constituent, — here oxygen serves the purpose, — secure the liberation of the element. Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

Electrolysis of Chlorides. — Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when a current of electricity is passed through the aqueous solution. They yield chlorine at the positive electrode. The other constituent, the hydrogen (Fig. 42), manganese, or whatever it may be, is liberated at the negative wire. To decompose hydrochloric acid an electromotive force of at least 1.31 volts is required. Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas: Cl_2 (dslvd) $\rightleftarrows$ Cl_2 (gas). The shape of the apparatus keeps the two products from mingling. The presence of the chlorine in the liquid at the positive end may be shown by a suitable test (pp. 66 and 114).

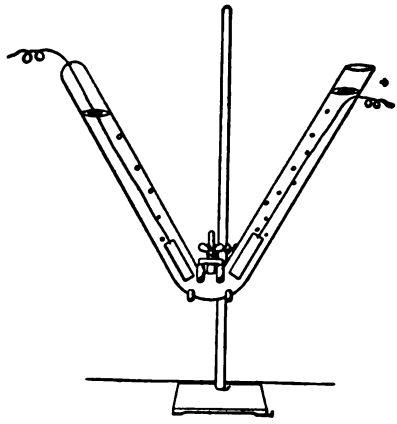

FIG. 42.

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. Electrodes of artificial graphite are used, as most other conductors unite with the chlorine. The potassium or sodium, as the case may be, travels towards the negative electrode, but is not liberated. Instead, potassium or sodium hydroxide accumulates in the solution round the plate and hydrogen escapes. The chlorine is released at the positive electrode, as usual. The hydroxide and the chlorine both find chemical applications. The chlorine is either liquefied by compression in steel cylinders or employed at once for making bleaching powder (*q.v.*).

Action of Free Oxygen on Chlorides. — Sodium chloride is the cheapest source of chlorine, but oxygen does not interact with it even at a high temperature. By treating the sodium chloride with sulphuric acid, therefore, the chlorine is first transferred into combination with the hydrogen of the acid. The details of this action are described below (see p. 117). In order to liberate chlorine from

the hydrogen chloride, we may then combine the hydrogen with oxygen obtained from the air. The action is in accordance with the equation:

$$2HCl + O \rightleftarrows H_2O + 2Cl.$$

The two gases interact so slowly, however, that a catalytic agent must be employed. The mixture of air and hydrogen chloride is passed over pieces of heated pumice-stone or broken brick previously saturated with cupric chloride solution. A temperature of 370°–400° is used. Furthermore, the action is reversible and equilibrium is reached when 80 per cent of the hydrogen chloride has been decomposed. Hence 20 per cent of this gas passes on unchanged. In the product, the chlorine is mixed with steam and with a very large volume of nitrogen which entered with the oxygen, as well as with unused hydrogen chloride, so that, for making the pure substance, this method (Deacon's process) is quite unsuitable.

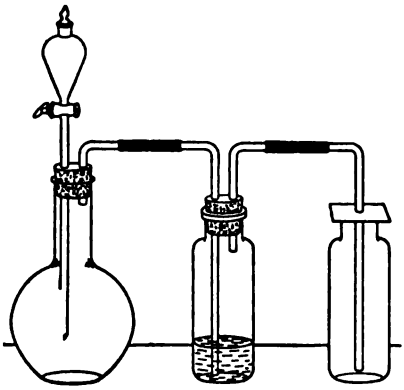

FIG. 43.

The above action is spoken of as an oxidation. It is true that no oxygen is actually introduced into the hydrogen chloride as a whole. The removal of hydrogen from combination with the chlorine is, however, the first step towards the introduction of oxygen into combination with the latter, and is essentially an oxidation.

Action of Combined Oxygen upon Chlorides. — The best laboratory method for making chlorine is to place some solid potassium permanganate in a flask, arranged like that in Fig. 43. Concentrated commercial hydrochloric acid (an aqueous solution of hydrogen chloride), diluted with one-third of its volume of water, is allowed to fall upon the compound drop by drop from the

dropping funnel. The action is very rapid, the acid is exhausted almost as fast as it falls, and so the stream of gas can be stopped by simply closing the stopcock. The gas is passed through a washing bottle containing water, in order to remove some hydrogen chloride which may be carried over. It may be dried, if necessary, in a second washing bottle containing concentrated sulphuric acid. It cannot be collected over water on account of its solubility, so that jars are usually filled with it by downward displacement of air.

The skeleton equation (p. 42) here is:

$$KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl.$$

The O_4, being all converted into water, requires 8H, and therefore 8HCl, for the action. The two metals, potassium and manganese, give their respective chlorides, KCl and $MnCl_2$. This uses 3Cl, and hence 5Cl remains over to be liberated:

$$KMnO_4 + 8HCl \rightarrow 4H_2O + KCl + MnCl_2 + 5Cl.$$

The combined oxygen of the permanganate has oxidized the hydrogen chloride, just as did the free oxygen in Deacon's process.

Many other compounds of oxygen with metals interact with hydrochloric acid to give free chlorine. Lead dioxide PbO_2, potassium chlorate $KClO_3$, potassium dichromate $K_2Cr_2O_7$, and manganese dioxide MnO_2, are of this nature. The last, being inexpensive, is commonly used in making chlorine. Being an insoluble substance, however, the manganese dioxide acts much more slowly than does the potassium permanganate, which is soluble. A large amount of the materials, and the aid of heat, are required to secure a rapid stream of chlorine.

The action of manganese dioxide upon hydrochloric acid is an instructive one. It is a **general rule**, of which we shall meet many applications, that **when an acid interacts with an oxide of a metal**, there are two constant features in the result, namely: (1) **The oxygen of the oxide combines with the hydrogen of the acid to form water**, and (2) **the metal of the oxide combines with the acid radical of the acid** according to the valences of each. Here the skeleton equation should be, $MnO_2 + HCl \rightarrow H_2O + MnCl_4$. For O_2, to form water, 4HCl is required, and the product is $2H_2O$. Hence the equation might be:

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_4.$$

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117), along with
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ars more complex, but is simply a combination of the two chem- changes, and is represented by the equation:

$$O_2 + 2NaCl + 3H_2SO_4 \rightarrow 2H_2O + 2NaHSO_4 + MnSO_4 + 2Cl.$$

3 mixture cannot be used with potassium permanganate, as losion is apt to occur.

Physical Properties. — Chlorine differs from the gases we have countered so far in having a strong greenish-yellow tint (Gk. ωρός, pale green), a fact which gave rise to its name, and having a werful, irritating effect upon the membranes of the nose and throat.

Density (H = 1), 35.79	Boiling-point (liq.), − 33.6°
Weight of 1 l., 3.220 g.	Melting-point (solid), − 102°
Sol'ty in Aq (20°), 215 vols. in 100	Vap. tension (liq.) 0°, 3.66 atmos.
Crit. temp., + 146°	Vap. tension (liq.) 20°, 6.62 atmos.

Since a liter of air weighs 1.293 g., chlorine is two and a half times eavier. In solubility it stands between slightly soluble gases, like xygen and hydrogen, and those which are extremely soluble. It an be collected over hot water or a strong solution of salt.

Chlorine was first liquefied by Northmore (1805). It forms a yellow liquid which, contained in steel cylinders lined with lead, is now an article of commerce. On being cooled below − 102°, it gives a pale-yellow solid.

Chemical Properties. — Chlorine is at least as active a substance as is oxygen. It presents a more varied array of chemical properties than does that element.

1. Chlorine **unites directly with many elements.** A jet of hydrogen burns vigorously in chlorine, producing hydrogen chloride. The union of the gases, when a mixture of them is kept cold and in the dark, is too slow to be perceived. On exposure to diffused light, however, they unite slowly, while a sudden flash of sunlight or the burning of a magnesium ribbon causes instant explosion. The function of the light here is entirely different from that in the decomposition of silver chloride (pp. 9, 13). In the latter case light was used to maintain the change, which comes to a stop whenever the light is withdrawn. The action was endothermal and consumed energy. The union of hydrogen and chlorine is highly exothermal, and a minimum of light only is needed to start it (pp. 54, 55).

Sodium burns in chlorine, producing a cloud of white particles of sodium chloride. Copper in the condition of thin leaf, commonly used for gilding (Dutch-metal), catches fire spontaneously when thrust into the gas. Phosphorus burns in it with a rather feeble light, producing primarily phosphorus trichloride PCl_3, a liquid (b.-p. 74°). If excess of chlorine is present, then, as the trichloride cools, it combines to form the solid pentachloride PCl_5. Almost all the more familiar elements unite directly with chlorine to form chlorides. The exceptions are, nitrogen, oxygen, carbon, and the helium group of elements (p. 49). Compounds with all but the last may be obtained as products of more complex interactions, however. Some elements, like phosphorus, form more than one chloride.

Carefully dried substances, even when heated, unite slowly or, to all appearance, not at all with dry chlorine. The introduction of a drop of water, however, into a remote part of the apparatus at once supplies the trace of moisture which seems to be necessary to facilitate the chemical change. The water is a catalytic agent, and we regard it as simply hastening an action which otherwise is vanishingly slow (p. 54).

2. Chlorine, like sodium (p. 66), **may also displace elements which are already in combination.** Thus, when turpentine ($C_{10}H_{16}$) is poured over a strip of paper and is then immersed in a jar of chlorine, a violent action takes place, and an immense cloud of finely divided carbon bursts forth. The heat of the action, as it starts, vaporizes the turpentine, and the hydrogen in the latter unites with the chlorine forming hydrogen chloride, while the carbon is set free: $C_{10}H_{16} + 16Cl \rightarrow 16HCl + 10C$.

The action of chlorine on potassium iodide, dry or in solution, is of this kind, and furnishes the commonest **test** (p. 66) **for free chlorine.** The chlorine simply takes the place of the iodine ($KI + Cl \rightarrow KCl + I$), and the latter is liberated. Iodine, when moist, is deep brown in color, and the amount liberated by a large quantity of chlorine may easily be seen. Yet, it is an advantage so to arrange a test that it may be as **delicate** as possible, that is, may give a plainly visible result with the minimum of material. In this case, much starch emulsion and a little potassium iodide are employed. Strips of filter paper dipped in this mixture, when brought into a gas containing even a trace of free chlorine, show a deep-blue color (see Iodine). *Combined chlorine, as in a chloride, has no effect upon starch.*

3. When actions like that on turpentine are moderated by proper means, the decomposition is not so complete. If methane (marsh gas, CH_4) is mixed with chlorine and exposed to sunlight, a slower action occurs, of which the first stage consists in the removal of one unit weight of hydrogen and the **substitution** of chlorine for it according to the following equation:

$$CH_4 + 2Cl \rightarrow CH_3Cl + HCl.$$

The process may continue further by the substitution* of chlorine for the units of hydrogen one by one until carbon tetrachloride (CCl_4) is finally formed.

A most interesting and important action of this class occurs when chlorine is dissolved in water. A small part of the chlorine interacts with a little of the water, the element being substituted for one-half of the hydrogen:

$$2Cl + HOH \rightarrow HOCl + HCl. \qquad (1)$$

Only *traces* of hydrogen chloride and hypochlorous acid are produced, however, and a state of equilibrium is reached. The change comes quickly to a standstill, because the products interact even more vigorously to reproduce chlorine and water:

$$HCl + HOCl \rightleftarrows 2Cl + H_2O, \qquad (2)$$

the interaction being reversible (p. 46). This interaction of chlorine and water (1), slight as it is, is of importance on account of the instability of the hypochlorous acid (*q.v.*) which it produces. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is produced: $HClO \rightarrow HCl + O$. Since this removes the substance on whose interaction with the hydrogen chloride in (2), the reversal of (1) depends, the latter action proceeds under continuous illumination gradually to completion.

* **Substitution** resembles displacement (p. 68) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But *the latter is not liberated:* it combines with another unit of chlorine. *Double* decomposition the action is not, because elements do not decompose. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon.

Hence the aqueous solution of chlorine must be kept in the dark, since otherwise a dilute solution of hydrogen chloride alone remains.

The reader should note here the displacement of the equilibrium, a chemical one in this case, in consequence of the annulment of one of the opposing tendencies (p. 91). Through the destruction of the hypochlorous acid, one of the tendencies, namely that represented in the forward direction of (2), becomes inoperative.

4. Chlorine may simply add itself to a compound. Thus, one of the oxides of carbon, carbon monoxide CO, when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b.-p. 8.2°) known as phosgene $COCl_2$.

Chemical Relations of the Element.* — In the formation of chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, univalent (p. 70). It never shows any higher valence than this, save in its oxygen compounds (see Chap. xvi). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a non-metal (p. 82). It belongs to that group of the non-metals called the halogens (*q.v.*), as a consideration of some others of its relations will show (see Chap. xiv).

Uses of Chlorine. — Large quantities of chlorine are manufactured for the preparation of bleaching materials and disinfecting agents. In disinfection, the minute germs of disease and putrefaction are acted upon either by the chlorine or by the hypochlorous acid formed by its interaction with water, and instantly their life is destroyed. One of the processes for the extraction of gold involves an action of chlorine gas upon the material after it has received preliminary treatment. A chloride of gold is formed, which can be dissolved out of the matrix by means of water, and the metallic gold is afterwards precipitated from the solution.

* In accordance with the distinction that must be drawn (p. 20) between the element as a variety of matter *in combination*, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element, as a class, from, or relate them as a class to the compounds of other elements will then appear in a separate section under the title "Chemical relations" (see pp. 157, 172).

Hydrogen Chloride HCl.

Preparation from Sodium Chloride. — As we have seen, the direct union of hydrogen and chlorine produces a gas, hydrogen chloride (HCl). For the purpose of preparing this gas, however, some more easily managed method will naturally be employed.

In commerce large quantities of hydrogen chloride are obtained as a by-product in connection with the manufacture of soda. The same materials are commonly employed in the laboratory. Common salt is treated with concentrated sulphuric acid at a gentle heat. Effervescence is seen and hydrogen chloride is given off, while a compound known as sodium hydrogen sulphate (sodium bisulphate or acid sulphate) remains behind. The action is represented by the equation:

$$NaCl + H_2SO_4 \rightarrow HCl\uparrow + NaHSO_4. \qquad (1)$$

The apparatus used in the preparation of chlorine (Fig. 43) may be employed. On account of its extreme solubility, the gas is not washed in water, however. For the same reason it must be collected by downward displacement of air, or over mercury.

The above statements apply to the action when no high temperature is employed. If, however, a larger proportion of salt is used and a sufficiently high temperature produced by artificial heating, then neutral sodium sulphate is formed according to the equation:

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4. \qquad (2)$$

The former action is that which occurs under the conditions used in the laboratory. The latter is the action which, with furnace heat, is employed in commerce, since it is for the purpose of making sodium sulphate (Na_2SO_4), from which sodium carbonate is afterwards to be prepared, that the operation is undertaken. The hydrogen chloride passes through a tower, down which water trickles over lumps of coke, and is dissolved. The aqueous solution is called hydrochloric acid, or, in commerce, muriatic acid.

Interaction of Acids and Chlorides. — It should be noted:

1. That the above-mentioned actions are both *double decompositions.*

2. That when any acid is used in a double decomposition, *another acid* must result, by transfer of the radical hydrogen which all acids

contain. For example, with ammonium nitrate and sulphuric acid we obtain nitric acid:

$$(NH_4)NO_3 + H_2SO_4 \rightarrow HNO_3 + (NH_4)HSO_4.$$

3. That hydrogen chloride, in particular, can be formed by double decomposition of any acid with *any substance containing the chloride radical* (Cl).

To make hydrogen chloride, use of an acid that can be obtained *free from* any large amount of *water* gives the best result (see below). Thus, concentrated phosphoric acid with any chloride will give a change parallel to those described above. With potassium chloride this action would be, $KCl + H_3PO_4 \rightarrow HCl\uparrow^* + KH_2PO_4$ (primary potassium phosphate).

The Kinetic Hypothesis Applied to the Interaction of Sulphuric Acid and Salt. — One who has used the above-described method for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experiment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a saturated solution of sodium hydrogen sulphate in water and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:

$$NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl\downarrow.^* \qquad (3)$$

Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal success. In fact, this chemical interaction is not only reversible (pp. 46, 51, 115), but can be carried to completion in either direction. It is only in presence of a large amount of water that it stops midway in its career and is valueless for securing a complete transformation in either direction:

$$NaHSO_4 + HCl \rightleftarrows H_2SO_4 + NaCl.$$

In an action which is reversible, if the products remain as perfectly

* The arrow directed downwards indicates elimination of a substance by precipitation, that directed upwards, escape as a gas or solution of a solid.

mixed and accessible to each other as were the initial substances, their interaction will continually undo a part of the work of the forward direction of the change. Hence, in such a case the reaction must, and does, come to a standstill while as yet only partly accomplished (*cf.* p. 115); but this was not the case with actions (1) and (3). Let us examine the means by which the premature cessation of each was avoided.

In equation (1) the salt dissolved to some extent in the sulphuric acid, NaCl (solid) $\rightleftarrows$ NaCl (dslvd), and so, by contact of the two kinds of molecules, the products were formed. On the other hand, the hydrogen chloride, being insoluble in sulphuric acid, escaped as fast as it was formed: HCl (dslvd) $\rightleftarrows$ HCl (gas). Hence, in that case, almost no reverse action was possible, and the double decomposition went on to completion. With all the sodium hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient re-interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.

In equation (3), on the other hand, the hydrogen chloride was taken *in aqueous solution*, and was kept permanently in full contact with the sodium bisulphate. It had therefore, in this case, every opportunity to interact with the latter and no chance of escape. Every molecule of each ingredient could reach every molecule of the other with equal ease. Furthermore, the sodium chloride produced as a result of their activity is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate: NaCl (dslvd) $\rightleftarrows$ NaCl (solid). But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. It was in a state of fine powder, it is true. But, in the molecular point of view, the smallest particle of a powder contains millions of molecules, and most of these are necessarily buried in the interior of a particle. Thus the sodium chloride was no longer able to interact effectively molecule to molecule with the other product, the sulphuric acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (3) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

This discussion is given to illustrate the displacement of a chemical

equilibrium, and to explain the method of preparing hydrogen chloride. It also throws an interesting light on chemical affinity, however. Considering action (1), by itself, we might reason that the hydrogen chloride was formed because the affinity of the hydrogen (H) for chlorine (Cl) was greater than for the sulphate radical (SO_4). But, if we did so, then in action (3) we should be compelled to reason similarly that the preponderance of affinity was just the opposite. In point of fact, no conclusion about relative affinity can be drawn from these actions. The effects of affinity are here entirely subordinated by the effects of a purely mechanical arrangement, depending on solubility. When the activities of the acids are properly compared, hydrochloric acid is found to be considerably more active than sulphuric acid.

Physical Properties.— Hydrogen chloride is a colorless gas, which produces a suffocating effect when breathed.

Density (H = 1), 18.23	Crit. temp., + 52°
Weight of 1 l., 1.64 g.	Boiling-point (liq.), − 83.7°
Sol'ty in Aq (0°), 50,300 vols. in 100	Melting-point (solid), − 110°

The gas is one-fourth heavier than air. On account of its great solubility it condenses atmospheric moisture into a fog of drops of hydrochloric acid. Both in the gaseous and liquefied states it is a nonconductor of electricity. Its heat of solution (p. 100) is 17,400 calories. On account of its high concentration, the saturated, aqueous solution may be looked upon as a mixture of liquefied hydrogen chloride and water.

When the *concentrated* aqueous solution is heated, it is the gas and not the water which is driven out, for the most part. When the concentration has been reduced to 20.2 per cent, the rest of the mixture distils unchanged at 110°. If a *dilute* solution is used, *water* is the chief product of distillation (about 100°), but gradually the boiling-point rises, and, when the concentration has reached 20.2 per cent once more, the same hydrochloric acid of constant boiling-point, as it is called, forms the residue.

Chemical Properties. Hydrogen chloride is extremely stable, as we might expect from the vigor with which the elements of which it is composed combine. On being heated to a temperature of 1800° it begins, however, to dissociate into its constituents.

In the chemical point of view, it is on the whole rather an indifferent substance. Hydrogen chloride (the gas) has no action upon any of the non-metals, such as phosphorus, carbon, sulphur, etc. Many of the metals, however, particularly the more active ones, such as potassium, sodium, and magnesium, decompose it. Hydrogen is

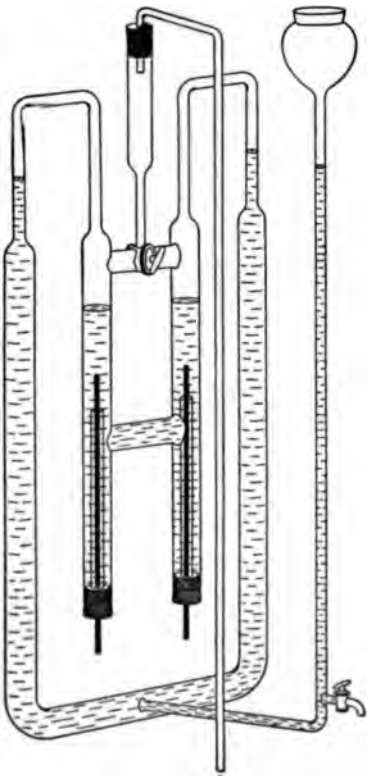


FIG. 44.

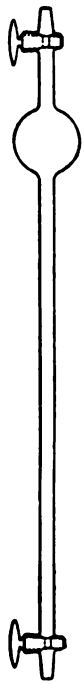


FIG. 45.

set free, and the chloride of the metal is formed ($K + HCl \rightarrow KCl + H$). Hydrogen chloride unites directly with ammonia gas to form solid ammonium chloride ($HCl + NH_3 \rightarrow NH_4Cl$). The liquefied gas has the same properties.

Composition.—The proportion of hydrogen to chlorine by weight in this compound is 1.008 : 35.45.

The proportion by volume in which the constituents unite, and the relation of this to the volume of the resulting hydrogen chloride, may easily be shown in several ways. The decomposition of the solution of hydrogen chloride in water by means of the electric current proves that the gases are liberated in equal volumes. Brownlee's apparatus for demonstrating this is shown in Fig. 44. The central part is the same as in Fig. 21, but, when the three-way stopcock is closed, the gases go to right and left, and displace the liquid in two outside tubes. The equal rate at which this takes place on both sides proves that the gases are generated in equal volumes.

In order to ascertain the relation between the volumes of the constituents and that of the product, we may unite the gases and find out whether any change in volume occurs. A tube with thick walls (Fig. 45) is filled with the mixed gases obtained by electrolysis. By dipping one end of the tube under mercury and opening the lower stopcock, it is seen that no gas leaves and no mercury enters. After the mixture has been exploded, by the light from burning magnesium, the same test is repeated with the same result. The pressure has therefore remained equal to that of the atmosphere. Hence there has been no change in volume as the result of the union. It appears therefore, that:

1 vol. hydrogen + 1 vol. chlorine → 2 vols. hydrogen chloride,

a result in harmony with Gay-Lussac's law (p. 84).

Chlorides. — The chlorides are described individually under the other element which each contains. For the present we simply add to the statement on p. 118 that the majority of the chlorides of the metals are easily soluble in water. The chief exceptions are silver chloride ($AgCl$), mercurous chloride (calomel, $HgCl$), cuprous chloride ($CuCl$), and lead chloride ($PbCl_2$). The last of these is on the border line as regards solubility. An appreciable amount dissolves in cold water, and a considerable amount in boiling water (see Table of solubilities, inside the cover at the front of this book).

The various modes of preparing chlorides are enumerated in the next section.

Chemical Properties of Hydrochloric Acid. — The solution of hydrogen chloride in water is an entirely different substance in its chemical behavior from hydrogen chloride. It is strongly acid, turn-

ing litmus red. The gas and liquefied gas have no such property. The solution **conducts electricity**, as we have seen, very well, and is decomposed in the process, while the gas and the liquefied gas are practically nonconductors.

Many **metals**, when introduced into hydrochloric acid, **displace the hydrogen** (p. 65), and form the chloride of the metal. In the case of zinc the action was represented by the equation:

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H.$$

The aqueous solution of hydrogen chloride **interacts** rapidly **with** most **oxides and hydroxides of metals**, as, for example, those of zinc:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O,$$
$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O.$$

Here no free hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained. It may be noted, in passing, that all acids behave in a similar manner towards oxides and hydroxides, giving water and a compound corresponding to the chloride (*cf.* p. 111). Dilute sulphuric acid, for example, gives sulphates.

In the two preceding paragraphs, three kinds of actions, each constituting a different **mode** of **preparing chlorides**, have been mentioned incidentally. There are two others which we have already encountered. The simplest is the direct union of the element with chlorine ($Zn + 2Cl \rightarrow ZnCl_2$). The other method is illustrated in the case of the precipitation of silver chloride (p. 8). Here the formation of the chloride occurred by exchange of another radical for chlorine ($AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$). The insoluble chlorides (p. 122) can be made conveniently by this plan. The formation of the precipitates, for example that of silver chloride, is used as a **test** for the presence of a soluble chloride in the solution.

The solution of hydrogen chloride in water sold in commerce is known by the name of **muriatic acid** (Lat. *muria*, brine). It is a yellow liquid which contains a number of impurities. The most common are, ferric chloride, which is responsible for part of the yellow tint, some yellow organic coloring material, arsenious chloride, and free chlorine. The acid frequently gives a residue when evaporated, and this must of course represent some impurity. It is sometimes

adulterated with calcium chloride, since the price obtained depends upon the specific gravity of the solution, and this may be raised by dissolving calcium chloride in it.

Classification of Chemical Interactions and Exercises Thereon. — So far we have defined ten more or less distinct kinds of chemical change, seven differing in mechanism: **Combination** (p. 9), **decomposition** (p. 10), **dissociation** (p. 81), **displacement** (p. 68), **substitution** (p. 115), **double decomposition** (pp. 10, 68), and **internal rearrangement** (p. 10); and three others: **oxidation** (pp. 52, 75, 110, 112), **reduction** (pp. 53, 75), and **electrolysis** (pp. 13, 64). Illustrations of all but one of these will be found in the present chapter. Some actions belong to one of the first seven, and also to one of the three other classes. The ability readily to classify each phenomenon, as it comes up, requires precisely that grasp of the framework of the science which the reader must seek speedily to attain. For example, let him classify the following actions: 1. action of potassium on water; 2. of heat on potassium chlorate; 3. of chlorine on metals; 4. of chlorine on turpentine; 5. of chlorine on potassium iodide; 6. of chlorine on methane; 7. of carbon monoxide and chlorine; 8. of sunlight on hypochlorous acid; 9. of sulphuric acid on salt; 10. of zinc oxide and hydrochloric acid; 11. of zinc on hydrochloric acid.

12. In the interactions of potassium permanganate and of manganese dioxide, respectively, with hydrochloric acid, what fractions of the whole chlorine are liberated? What are the commercial advantages of the use of salt and sulphuric acid with the manganese dioxide?

13. In view of the explanations given, can you define the general nature of the substances (p. 111) which may be used to oxidize hydrochloric acid?

CHAPTER XII

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

AVOGADRO'S hypothesis (p. 89) has proved to be by far the most suggestive and fruitful of all the conceptions developed from the kinetic-molecular hypothesis. We are now in a position to discuss several of its most important applications. To speak in terms of the hypothesis, these concern more particularly the measurement of the relative weights of the molecules of different gaseous substances, and the determination of the most convenient magnitudes for the chemical unit weights (atomic weights; *cf.* p. 36).

Meaning of Avogadro's Hypothesis. — First, we must understand clearly what is implied in the statement that: In equal volumes of all gases, at the same temperature and pressure, there are equal numbers of molecules. It means that, for instance, at 100° and 760 mm., in all specimens of gases the average spacing of the molecules is identical. This condition is independent of the nature of the gas — for example, whether it is a simple or a compound substance, like oxygen and carbon dioxide respectively, or a mixture, like air. It means that when, at some fixed temperature, we fill the same vessel with a number of different gases or gaseous mixtures successively, the number of molecules that it will hold at a pressure, say, of one atmosphere will always be the same. If we take care to keep temperature and pressure the same, the equality in the number of molecules that will enter the jar will take care of itself automatically. In what follows, to avoid continual repetition, it is to be assumed that temperatures and pressures are equal unless the contrary is expressly stated.

MOLECULAR WEIGHTS.

The Relative Weights of the Molecules. — According to Avogadro's hypothesis, vessels of equal size filled with different gases contain equal numbers of gaseous molecules. Now equal volumes of different gases differ very markedly in weight, or, in other words,

the densities of various known gases cover a wide range of values. Thus, hydrogen is the lightest of all, chlorine is more than thirty-five times, mercuric chloride (corrosive sublimate) vapor over one hundred and thirty-four times as heavy. Since these different weights of equal volumes represent the weights of equal numbers of molecules, the difference must be due to the differing weights of the molecules themselves. The **densities of gases, therefore, may be taken as measures of the relative weights of their individual molecules.** The extreme significance of this inference in chemistry will appear as we elaborate upon it.

The various scales on which the densities of gases may be calculated, such as the weights of one liter of each gas, or the weights of volumes equal to that of one gram of air, are illustrated in the first two columns of the following table:

	Weight of One Liter, 0° and 760 mm.	Density, Air = 1.	Molecular Weight, Ox. = 32.
Hydrogen	0.090	0.0696	2.016
Oxygen	1.429	1.105	32.00
Chlorine	3.166	2.449	70.90
Hydrogen chloride	1.628	1.259	36.458
Carbon dioxide	1.965	1.520	44.00
Water	0.8045	0.622	18.016
Mercury	8.932	6.908	200.0
Mercuric chloride	12.097	9.354	270.90
Air	1.293	1.00	28.955

The values for water (b.-p. 100°), mercury (b.-p. 357°), and mercuric chloride (b.-p. 300°) are measured at high temperatures and reduced by rule (p. 62) to 0° and 760 mm. All the numbers in the first two columns, as they stand, are purely physical in derivation. Those in the second column are obtained from those in the first by using the proportion:

1.293 (wt. 1 l. air) : 1.00 (air = 1) : : wt. of 1 l. any gas : x (dens. of that gas).

The last column will be explained presently. Since the numbers in the first column apply to equal volumes (1 l.), and those in the second stand in constant ratios to them, the weights in the second column represent equal volumes also. In the second, the volume

is $\frac{1}{1.993}$ l. The values in *either* one of the columns represent the relative weights of the molecules of the various substances (see Exercise 1 in this chapter).

Molecular Weights. — The foregoing section shows that, provided a substance is a gas or can be volatilized, the relative weight of its molecules, compared with those of other volatile substances, can be ascertained. To save words, the *relative weight of the molecules* of a substance is called the **molecular weight** of the substance. Since the absolute weights of molecules cannot be determined, the next question which arises is as to the choice of an appropriate unit, and therefore an appropriate scale for these relative weights, or molecular weights. Now the numbers already given, in the first two columns of the table, are purely physical data and, as they stand, lack direct relation to chemical facts. A set of *chemical* numbers is required for chemical purposes. We, therefore, proceed next to show how the required relation between the relative weights of molecules and chemical facts can be established.

Chemistry deals with chemical combination, and most substances are compounds. If we fix our attention, then, first, on compound substances and their molecules, we perceive at once that the molecules of a compound substance must contain two or more elements in definite proportions by weight. We may therefore extend the molecular hypothesis by supposing that a molecule is composed of smaller parts, which we call **atoms**. The atoms will be elementary. Thus the molecule of the compound will contain *one or more atoms of each of the component elements.* This conception, the starting-point of the atomic hypothesis, is elaborated in the next chapter. Its introduction in the present connection, however, at once suggests two ideas. In the first place, since we can now determine the relative weights of molecules, we should also somehow be able, with the help of the combining proportions, to determine the relative weights of the *atoms* of the elements. If these relative weights of atoms are properly determined, then the weights of the atoms, when added together, should give the weight of the molecule. Thus, — and this is the second idea, and the one of most immediate use to us, — the scale for relative weights of molecules must be chosen with reference to the scale for relative weights of the atoms, so that the former weights may always include the latter. That is to say, the molecular weights

must be based upon the combining weights. This means that the scale must be such that no molecule of a compound of hydrogen shall receive a value so small that the proportion of hydrogen in it is less than 1.008. Furthermore, since the combining weight of oxygen is the standard for combining proportions, it is desirable to use this substance as basis of the scale of molecular weights. Now, as we shall find (see p. 131), it turns out that, to avoid obtaining proportions of hydrogen less than unity, we are compelled to take the scale 32 for the molecular weight of oxygen. Our *chemical* scale of densities is therefore calculated to the scale, **density of oxygen = 32.** This, then, is the answer to the problem with which the section opened. The third column of the table (p. 126) shows the results of recalculating the densities to this chemical scale. The proportion used is:

$$\text{Density of Ox.} : \text{Density of Substance} :: 32 : x.$$

Thus, if we take the densities from the first column, the value for water is found by the proportion, $1.429 : 0.8045 :: 32 : x$ ($= 18.016$). That is, we multiply the weight of a liter of the gas by 32/1.429 to get the molecular weight.

Since the gram is the unit of weight, 32 g. of oxygen, or 18.016 g. of water is called the **gram-molecular weight** of the substance. It will be noted that 32 g. is not the weight of *a* molecule of oxygen. It is the weight of a very large, and not exactly known number of molecules of oxygen. But, whatever that number of molecules of oxygen is, 18.016 g. of water contains the *same number* of molecules, and the other weights in the same column are weights of numbers of molecules equal to these. The term gram-molecular weight being somewhat ponderous, we abbreviate it to **molar weight**, and still further to **mole**. Thus, a *mole* of chlorine is 70.9 g. of the element, and a mole of hydrogen chloride is 36.458 g. of the compound.

The Gram-Molecular (Molar) Volume. — The weights in the last column of the table (p. 126) must represent equal volumes of the different gases. This follows from the fact that they are derived from the values in the first column by multiplying by a constant ratio (32/1.429), and the volume in the first column is always 1 liter. The actual dimension of this volume is evidently 32/1.429 liters, which is almost exactly 22.39, or in round numbers **22.4 liters.** This volume at 0° and 760 mm. holds 32 g. of oxygen, 70.9 g. of chlorine, 44.00 g. of carbon dioxide, or, in fact, the molar weight of any gaseous

substance. It is called, therefore, the **gram-molecular volume (G.M.V.)** or the **molar volume.** It may be defined as **that volume which contains one mole (gram-molecular weight) of any gas at 0° and 760 mm.** At other temperatures and pressures the G.M.V. has correspondingly different values.

The G.M.V. gives us a concrete conception of a molar weight. This volume is represented by a cube (Fig. 46) 28.19 cm. (or about 11.1 inches) high. Like any other volume, it holds the identical numbers of molecules of different gases.* Its capacity at 0° and 760 mm. is the number of molecules in 32 g. of oxygen. Hence, in terms of the hypothesis, the weight of any gas which fills it bears to 32 g. the same ratio as the weight of a molecule of that gas to the weight of a molecule of oxygen. We may, therefore, state the **method of finding the molar (gram-molecular) weight of a substance thus: Weigh a known volume of the substance, at any temperature and pressure at which it is gaseous, reduce this volume by rule to 0° and 760 mm., and calculate by proportion the weight of 22.4 liters** (see Exercises 1, 2, 3, 5).

FIG. 46.

That quantity of each substance which at 0° and 760 mm. would fill the G.M.V. cube is the unit quantity of the substance for all theoretical purposes in chemistry. It represents the relative weight of the molecules of the substance. We shall employ it at once for the purpose of determining the *relative weights of atoms*, or atomic weights.

* A common question is: Do not molecules of different substances differ in size, and will not the numbers required to fill the G.M.V. therefore be different? The answer is that the molecules are all so small compared with the spaces between them (at 760 mm.) that the distances from surface to surface are practically the same as from center to center. A G.M.V. of oxygen, when liquefied, gives less than 32 c.c. of liquid oxygen, or less than 1/700 of the volume as gas. And there are still spaces between the molecules of the liquid. It is only when gases are so severely compressed that the nearness of the molecules to one another approaches that found in the liquid condition that the effects of the bulk of the molecules becomes conspicuous, and a difference in the behavior of different gases is noticeable. But in the work discussed in this chapter, pressures over one atmosphere are not used.

Atomic Weights

Determination of the Atomic Weight of Each Element.— If the paragraphs dealing with combining weights are now re-read (pp. 31–38), it will be found that the foundations for a system of weights was worked out, but that no basis for *definitely fixing* the individual values was discovered. At the time, the only information we had was obtained by analyzing compounds and reasoning about the results, and evidently something more was needed for the absolute determination of the values. Thus on p. 35, the equally good standing of two different possible values for the combining weight of copper, namely 63.6 and 31.8, was brought out. The same dilemma would have occurred with every element which combines in two or more different proportions with any other, and therefore affects nearly the whole list. In the history of chemistry, the same uncertainty caused much controversy among chemists and, for years, endless confusion. It was only when the comparison of the combining weights with the relative weights of molecules was at last rigorously applied, in the fashion now to be shown, that perfect order in chemical weights and formulæ was finally achieved.

To determine the atomic weights, the plan of procedure is perfectly simple. In the preceding section we settled upon the chemical unit quantity of each substance. This is the quantity which, in the gaseous condition, would fill the G.M.V. (22.4 liters) at 0° and 760 mm. Now, we seek the chemical unit quantities of the elements combined in each substance. Evidently the logical and consistent plan must be to take the amount of each substance which fills the G.M.V. and find out how much of each element present is contained in this unit amount of the substance. In other words, to put the matter concretely, we imagine ourselves filling the cube (Fig. 46) with one compound after another, and in each case determining by analysis the weight of each constituent element present in a cube-full of the substance. To carry out this plan, two experimental operations are necessary with each substance:

First we determine the density, and this gives us the gram-molecular weight, *i.e.* the amount filling the cube. This shows the relative weight of a molecule of the substance, as compared with that of one molecule of oxygen.

Then we analyze the substance, and this gives us the quantity

of each constituent in the total gram-molecular weight, *i.e.* in the material filling the cube. This, in turn, shows the weight of the quantity of each element present in each molecule, relative to the weight of a molecule of oxygen.

For example, the cube holds 36.458 g. of hydrogen chloride, and this amount, when decomposed, yields 1.008 g.* of hydrogen and 35.45 g. of chlorine.

Finally, to determine the best combining weight for a given element, we repeat the two foregoing operations with as many different compounds of the element as possible, and then we examine the various quantities of the element found in the G.M.V. of the various compounds. From inspection of these quantities we quickly select the value of which all are multiples, by unity or some integral number. This value for the combining weight is the one accepted. In terms of the hypothesis, this is the weight of one atom of the element, compared with the weight of a molecule of oxygen, and molecules containing more than this proportion contain two, three, or more atoms of the element.

For example, if we are seeking the atomic weight of chlorine, we set down the result for hydrogen chloride just given. Then we take another compound of chlorine, say phosphorus oxychloride. We determine the weight of a measured volume of its vapor, at a properly chosen temperature and pressure, and the result gives us, by calculation, the molecular weight, *viz.* 153.35. That is, 153.35 g. of the substance would fill the cube, if it could be kept as vapor at 0° and 760 mm. And this amount of the substance contains 31 g. of the element phosphorus, 16 g. of the element oxygen, and 106.35 g. of the element chlorine. We then continue the processes described, using all the volatile compounds of chlorine. The involatile compounds (like common salt) must be set aside, for they cannot be vaporized, and therefore their molecular weights cannot be determined. When we have studied as many compounds as possible in this way, we find that there are different quantities of chlorine in our list, *but they are all integral multiples of* 35.45 *g.* In phosphorus

* It will be observed that if the unit for molecular weights had been less than the number of molecules in 32 g. of oxygen, then an equal number of molecules of hydrogen chloride would have contained less than 1.008 g. of hydrogen, and the atomic weight of this element would then have been less than unity.

oxychloride, for example, the quantity was 106.35, or 3 × 35.45. Hence 35.45 g. can be taken as the unit quantity, the atomic weight of the element chlorine. In terms of the hypothesis, this is the relative weight of an atom of chlorine, as compared with that of a molecule of oxygen, when the value 32 is assigned to the latter.*

In the following table a few sample results of the process just outlined are given. The first column contains the molar weight, *i.e.* the weight of the substance which occupies the G.M.V. cube. In the other columns are entered the weights of the various elements which together make up the total molar weight. To simplify the numbers, the value 1 is used for hydrogen, instead of 1.008.

Substance.	Molar Weight	Weights of Constituents in Molar Weight.						
		Hydrogen.	Chlorine.	Oxygen.	Phosphorus.	Carbon.	Mercury.	Molecular Formula.
Hydrogen chloride	36.45	1	35.45	...	...	...	...	HCl
Chlorine dioxide	67.45	...	35.45	32	...	...	...	ClO_2
Phosphorus trichloride	137.35	...	106.35	...	31	...	...	PCl_3
Phosphorus oxychloride	153.35	...	106.35	16	31	...	...	$POCl_3$
Phosphoric anhydride	284	...	...	160	124	...	...	P_4O_{10}
Phosphine	34	3	...	...	31	...	...	PH_3
Water	18	2	...	16	...	...	...	H_2O
Methane	16	4	...	...	...	12	...	CH_4
Acetylene	26	2	...	...	...	24	...	C_2H_2
Ethylene	28	4	...	...	...	24	...	C_2H_4
Formaldehyde	30	2	...	16	...	12	...	CH_2O
Acetic acid	60	4	...	32	...	24	...	$C_2H_4O_2$
Mercurous chloride	235.45	...	35.45	...	...	...	200	$HgCl$
Mercuric chloride	270.9	...	70.9	...	...	...	200	$HgCl_2$

* It should be noted that there is another unit quantity of chlorine, namely the molecular weight, or weight of the G.M.V. of the substance. This is the unit quantity of free chlorine. But we are dealing now with compounds, and proportions in combination, so that free, uncombined chlorine, and other elements in free condition do not interest us at present, and will be taken up later.

To contain similar data for all the volatile compounds of every known element, a huge table, of which this might be a small corner, would be required. With such a table at hand the atomic weight of each element could promptly be picked out. Thus, in the carbon column it would be found that all the weights of carbon were either 12 or integral multiples of 12, and this is therefore the atomic weight of carbon. Similarly the atomic weight of oxygen is 16,* of phosphorus 31, of mercury 200 (see Exercise 4).

When the atomic weights have finally been selected, we can go through the table and change all the numbers into multiples of the chosen atomic weights. Thus, for 70.9 we write 2×35.45, and for 106.35 we write 3×35.45, and so forth. The reader can prepare such a modification of the table. With this new form of the table before us, we can, finally, replace the atomic weights by the symbols which stand for them, writing, for 35.45, Cl, for 2×35.45, Cl_2, and so forth. The results of doing this in each line, *i.e.* for each substance, are collected at the ends of the lines in the last column of the table. The reader should himself repeat the substitutions of the symbols, and so verify the formulæ given. These formulæ, since they are based on the molecular weights, in such a way that when the numerical values are substituted for the symbols the total restores to us the molecular weight, are called **molecular formulæ.**

It will now be seen why the equivalents (pp. 36–37) were multiplied by various integers in making the chemical units. The equivalent of carbon was 3. That is to say, carbon and oxygen combine in the ratio 3 : 8 (in carbon dioxide), and carbon and hydrogen in the ratio 3 : 1.008 (in methane). But there is no compound of carbon whose molecular weight contains less than 12 parts of the element. It would thus lead to needless complication to take 3 as the unit amount of carbon, for *every* molecule would then contain four units, or some multiple of four, and every formula C_4 or some multiple of C_4. We choose the largest units of combining weight that we can, in order that the coefficients may be the smallest possible, and the resulting formulæ the simplest possible. Naturally the actual ratios remain the same. Thus, for carbon dioxide the ratio 3 : 8 is replaced by 12 : 32, or $12 : 2 \times 16$, or C : 2O, which has the same value.

* The difference between the unit quantity of oxygen in compounds (namely, 16) and the unit quantity of free oxygen (32) will be discussed presently.

As a **definition**, the **atomic weight of an element** may be stated to be: **The smallest of the weights of the element found in the molecular weights of all its volatile compounds**, so far as these have been examined. Since the atomic weight is always a multiple of the equivalent weight (by unity, or some other integer), it might also be defined as: The largest even multiple of the equivalent which can be contained in the molecular weights of all the volatile compounds of the element. The complete list of accepted atomic weights is printed on the inside of the cover at the back of this book.

Advantages of Atomic Weights over Equivalents.— Since the method of determining atomic weights depends on rather complex reasoning, and involves much experimental work, the question may be asked whether, when found, they are worth all the trouble. It is manifest that equivalents are much simpler in nature, and much more easily ascertained than atomic weights. It will be expected, therefore, that we shall be able to show that the units Na = 23, Cu = 63.6, Al = 27.1, C = 12, etc., give a better view of the relations of the elements than do the equivalents 23, 31.8, 9.03, and 3, respectively. Now, the **atomic weights** are as good as equivalent weights, for the purpose of acting as units, in terms of which to express combining proportions, and **possess**, besides, **several** (at least five) **important properties or uses which equivalent weights entirely lack.**

Of these valuable properties, the first two have been mentioned already:

1. Being very often themselves larger numbers than the equivalents, atomic weights are often multiplied by smaller coefficients (p. 133). This simplifies our equations.

2. The atomic weight of an element can have but one value, and is definitely determinable. Most equivalents have more than one value (p. 33).

3. The atomic weight of an element has a valence (p. 68), while equivalents are equi-valent. While valence is a helpful conception in all branches of chemistry, organic chemistry is especially indebted to the conception of the quadrivalence of carbon for much of its development and most of its organization. The full illustration of this point is beyond the limits of the present book.

4. The periodic system (*q.v.*), the basis of a plan for classifying

the properties of all chemical substances, is founded upon the atomic weights.

5. Dulong and Petit's law is based upon atomic weights. This law furnishes also an alternative means of determining atomic weights that has frequently rendered valuable service, and on this account forms the subject of the next section.

Dulong and Petit's Law, an alternative Means of Determining Atomic Weights. — It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the **atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases.** In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The table, in which round numbers have been used for the atomic weights, shows that the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Product.	Element.	Atomic Wt.	Sp. Ht.	Product.
Lithium . . .	7	.94	6.6	Iron	56	.112	6.3
Sodium	23	.29	6.7	Zinc	65.4	.093	6.1
Magnesium . .	24.4	.245	6.0	Bromine (Solid)	80	.084	6.7
Silicon	28.4	.16	4.5	Gold	197	.032	6.3
Phosphorus (Yellow)	31	.19	5.9	Mercury (Solid)	200	.0335	6.7
Calcium . . .	40	.170	6.8	Uranium . . .	238.5	.0276	6.6

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise equal weights of the various elements through one degree. Now these *equal weights* contain fewer chemical units in proportion as the chemical unit weight is greater. Hence this law may be put in the form: **Equal amounts of heat will raise atomic weights of all elements through equal intervals of temperature.**

This being true, the equivalents, if used instead of the atomic weights, must give widely varying products. The quantities of heat required to raise equivalent weights through one degree are either equal to, or are fractions of, those required for the atomic weights,

according to the valence of the element. Hence the law applies only to atomic weights, and not to equivalents.

It will be seen at once that although the law of Dulong and Petit is purely empirical, it may nevertheless be **used for fixing the atomic weight of an element of which no volatile compounds are known.** We can always measure the equivalent with considerable exactness, and, when this has been multiplied by the specific heat of the free substance, we can see at a glance what integral factor will raise the product to the neighborhood of 6.4. For example, analysis shows us that in calcium chloride the proportion of chlorine to calcium, using the known atomic weight of chlorine as one term of the proportion, is 35.5 : 20. If calcium is univalent, 20 is its atomic weight. If it is bivalent, two units of chlorine are combined with 40 parts of calcium, and 40 is its atomic weight. If it is trivalent, three units of chlorine are united with 60 parts of calcium, etc. All we learn in reference to the atomic weight of calcium from this analysis is that its value is 20 or some integral multiple of 20. Nor can we fix the upper limit, for we are unable to obtain the weight of a known volume of calcium chloride vapor and so determine the molecular weight. But the specific heat of solid calcium being 0.170, we multiply this number by 20, and get the product 3.4. This is only half large enough, so we assume that 40 is a more probable value for the atomic weight of calcium. The product is then 6.8, which agrees fairly well with the average for other elements. We decide, therefore, that the symbol Ca shall represent forty parts by weight. The formula of calcium chloride is therefore $CaCl_2$, and calcium is bivalent.

Molecular Formulæ

Molecular Formulæ of Compounds. — If the molar formulæ in the table (p. 132) be examined it will be observed that several are not in their simplest terms. Thus, the formula of acetylene is C_2H_2. The formula CH would represent the composition of the substance equally well, for 12 : 1 is the same as 24 : 2. But the formula CH gives a total of only 13, while C_2H_2 shows the total weight of the molecule to be 26 and records for us therefore *the weight of the G.M.V.*, as well as the composition of the substance. And we shall find this additional property, peculiar to the molecular formula, to be a feature of the greatest practical value. Some of the practical uses of this improvement in our formula will be illustrated in this chapter, and

there is an example of one of them in the table itself. Thus, the molecular formula of acetic acid is $C_2H_4O_2$, and not the simpler, identical proportion CH_2O. The latter is the molecular formula of a totally different substance, formaldehyde, now much used as a disinfectant. The vapor of this substance has only half the density of acetic acid vapor, and this fact, recorded in the formula, helps to remind us that the substances are different. Still another substance of the same composition is fruit sugar (dextrose), $C_6H_{12}O_6$ (see Exercise 12). In addition to this and other practical advantages, molecular formulæ satisfy also the claim of logical consistence. If the symbols represent the atomic weights, the formulæ should be constructed so as to represent the molecular weights.

Molecular formulæ like C_2H_2 and $C_2H_4O_2$ are easily interpreted in terms of the atomic hypothesis. C represents one atom of carbon and H, one atom of hydrogen. But there is no reason why a molecule of acetylene should not contain two atoms of each kind. Similarly, the molecule of formaldehyde contains four atoms (CH_2O), and one of acetic acid eight atoms ($C_2H_4O_2$), and one of dextrose twenty-four atoms ($C_6H_{12}O_6$), although the relative numbers of each kind are the same. Indeed this hypothesis helps to clear the matter up, for chemists go so far as to account for the chemical behavior of the substances by an imagined geometrical arrangement of the atoms in their molecules, and these three kinds of molecules are supposed to differ in structure as well as in the number of atoms they contain.

The Molecular Weights and Formulæ of Elementary Substances.—The following table gives the densities of some elementary substances, including those of which the substances last discussed are compounds. The first column shows the atomic weight, which in each case is the minimum weight of the element found in a G.M.V. of any compound. For example, 16 g. of oxygen and 35.45 g. of chlorine are the weights in the amounts of water vapor and hydrogen chloride, respectively, which fill the cube (22.4 liters). The symbol, in the next column, stands for this quantity and occurs in many formulæ, such as H_2O and HCl. It represents the combining unit or atom. In the third column is given the density of the free, elementary substance. This weight of the simple substance fills the G.M.V. and is the molecular weight. It shows the weight of the molecule relative to the weights of the other molecules in the same

column, and to the weights of the atoms in the first column. In the last two columns are given the densities resolved into multiples of the atomic weights and the corresponding formulæ.

	Atomic Weight.	Symbol.	Density O = 32.	Density Factorized.	Formula of Free Element.
Oxygen	16.00	O	32.00	2×16.00	O_2
Hydrogen	1.008	H	2.016	2×1.008	H_2
Chlorine	35.45	Cl	70.90	2×35.45	Cl_2
Phosphorus	31.0	P	124.0	4×31.0	P_4
Mercury	200.0	Hg	200.0	1×200.0	Hg
Ozone	16.00	O	48.00	3×16.00	O_3
Cadmium	112.4	Cd	112.4	1×112.4	Cd
Potassium	39.15	K	39.15	1×39.15	K
Sodium	23.05	Na	23.05	1×23.05	Na
Zinc	65.4	Zn	65.4	1×65.4	Zn

The reader cannot fail to note a striking peculiarity. In the case of chlorine the molecular weight is 70.9, while the atomic weight is 35.45. With hydrogen and oxygen, also, the molecular weight contains two atomic weights. Yet this is not a general rule, for with mercury and several other elements the molecular and atomic weights are alike, while with phosphorus the molecular is four times the atomic weight. Evidently there is no rule, and each element has to be subjected to separate experimental study. The result is that for *free, elementary chlorine we use the molecular formula* Cl_2, for *free hydrogen* H_2, for *elementary, uncombined oxygen* the formula O_2. For a substance like phosphorus, which is not a gas and is not often used as a vapor, the formula P is commonly employed by chemists, to avoid the larger coefficients which P_4 introduces into equations, although theoretically the latter formula would be the strictly correct one.

The case of oxygen demonstrates clearly the necessity of using molecular formulæ, even for simple substances. The table shows *two* substances containing nothing but oxygen. Ozone (*q.v.*) has a molecular weight 48, being a gas exactly one-half heavier than ordinary oxygen. Its formula, therefore, is O_3, while that of oxygen is O_2. Oxygen and ozone are entirely different chemical individuals. The latter has, for example, a strong odor and is much more active.

Thus polished silver remains bright indefinitely in pure oxygen, but oxidizes quickly when placed in ozone.

To avoid a common error, the reader should note that to learn the atomic weight of an element, we do *not* measure the molecular weight of the simple substance. The molecular weight of the elementary substance may be a multiple of the atomic weight, and we find out whether it is such a multiple only after the atomic weight has been determined. The atomic weight is the unit weight used in compounds, and can be ascertained only by a study of compounds. The molecular weight of the free element gives us only a value which we know must be a multiple of the atomic weight, by 1 or some other integer. Mol. Wt. = At. Wt. $\times$ x, where x is 1 or some other integer.

Further Discussion of the Molecular Formulæ of Elementary Substances. — Some further explanation may be required, to the end that the reader may be reconciled to accepting the formulæ Cl_2, O_2, and so forth. In the first place, he should note how these formulæ arose. If we accept Avogadro's hypothesis, and the inference from it to the effect that the densities of gases are in the same ratio as the weights of their individual molecules, then we cannot escape the conclusion to which measuring the relative densities of free chlorine and hydrogen chloride, for example, leads. The ratio of their densities is 70.9 : 36.45. That is to say, the relative weights of a molecule of chlorine and a molecule of hydrogen chloride stand in this ratio. The molecule of chlorine is nearly twice as heavy as the molecule of the compound, *and there cannot therefore be a whole molecule of chlorine in a molecule of hydrogen chloride.* In fact, we perceive at once that the molecule of hydrogen chloride must contain only half a molecule of chlorine (35.45), together with half a molecule of hydrogen (1). In other words, if the molecule of free chlorine were to be taken as the atom of the element, then the molecule of hydrogen chloride would contain only half an atom of chlorine, which would be contrary to our decision to take as atoms quantities which are not divided. So we choose the other horn of the dilemma, and say that the specimen of chlorine in the molecule of hydrogen chloride is a whole atom and that therefore the amount of chlorine in the molecule of free chlorine is two atoms, and its formula Cl_2. Similarly, the weight of hydrogen in the molecule of hydrogen chloride is 1.008, while that of the molecule of hydrogen is 2.016, so that

there are two atoms in the molecule of free hydrogen and its formula is H_2. Reasoning in like manner from the molecular weights of oxygen (32) and water (18) we reach the conclusion that the molecule of oxygen is diatomic (O_2).

Still another way of looking at the same facts may shed light on the matter. When hydrogen and chlorine combine, one volume of each of these gases gives two volumes of hydrogen chloride (p. 122). Let us imagine the experiment to be made with minute volumes holding one hundred molecules each:

Hydrogen Chloride			Hydrogen		Chlorine
100	100	came from	100	+	100

The 200 molecules of hydrogen chloride must contain at least 200 fragments of chlorine, since there is a sample in each molecule. Now the 200 fragments of chlorine came from a volume containing only 100 molecules of chlorine. Each of these must therefore have been split in the chemical action. Hence the molecules of free hydrogen and free chlorine contain at least two atoms. If we consider the molecular formula of a substance as representing one molecule (see below), the equation for this action is:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

There are two molecules on each side of the equation, and this corresponds with the fact that there is no change in the total volume. Again, we find that one volume of oxygen furnishes enough of the element for two volumes of water vapor (p. 84). We infer therefore that each molecule of oxygen is divided into two parts in the action. And in like manner, when we find that one volume of phosphorus vapor, in combination with six volumes of chlorine, gives *four* volumes of phosphorus trichloride vapor, we infer that every molecule of phosphorus furnished enough of the element for four molecules of phosphorus trichloride, and contained therefore four atoms (see Exercise 7).

$$P_4 + 6Cl_2 \rightarrow 4PCl_3.$$

The simple fact that hydrogen and oxygen, when mixed, do not combine (p. 74) may assist in reconciling us to the diatomic nature of their molecules. Some part of the mixture has to be heated

strongly to start the interaction. Now the molecular formulæ, H_2 and O_2, suggest that each gas is really in combination already (with itself), and they therefore explain to some extent the indifference of the gases towards one another. If the molecules were free atoms, they could not encounter one another continually as they move about, and yet escape combination as we observe that they do. We may imagine that the primary effect of heating is to decompose some of the molecules, and liberate hydrogen and oxygen in the atomic condition, and that the combination of these atoms starts the explosion of the whole mass. Of course this explanation is based upon our hypothesis and, as such, is of the same imaginary description as everything connected with that hypothesis. It cannot be verified by experiment.

Applications.

Applications: Interactions Between Gases. — According to Avogadro's hypothesis, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance from particle to particle would be the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus, in a mixture of hydrogen and chlorine, according to our hypothesis, neighboring molecules of hydrogen and chlorine simply exchange units, so that HH + ClCl becomes HCl + ClH. There being no alteration in the number of particles, no change in volume occurs. In the case of water, on the other hand,

$$\text{HH} + \text{OO} + \text{HH} \text{ becomes } \text{HOH} + \text{HOH}.$$

Since the oxygen molecules, which form a third of the whole, disappear into the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 85).

This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the

molecules themselves. We cannot perceive the individual molecules, but, in consequence of the spatial arrangement which we suppose them to observe, the change in the whole volume of a large aggregate of molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

Applications: Molecular Equations. — To utilize the foregoing considerations, chemists always employ in their equations the molecular formulæ for the gases and easily vaporized substances concerned. Thus far, we have used the equation:

	H	+	Cl	→	HCl,
WEIGHTS:	1.008		35.45		36.458

and the information it contained was exhausted when we had placed below the symbols the weights for which they stood. But the molecular equation is much more instructive. The following shows the interpretations to which the molecular equation is subject:

	H_2	+	Cl_2	→	2HCl.
WEIGHTS:	2.016 g.		70.90 g.		2 × 36.458 (= 72.916) g.
VOLUMES:	22.4 l.		22.4 l.		2 × 22.4 l.
MOLECULES:	1		1		2

The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at once into *volumes*, and questions about volumes can also be answered. Finally the relative numbers of each kind of molecules can be read from this equation, for the coefficients in front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood. The application of these properties of molecular equations is illustrated below. Before applying these equations, however, we must first learn how to make them.

To make a molecular equation, we first make an equation according to the rules already explained (p. 41). An equation like that given for the interaction of oxygen with hydrogen chloride (Deacon's process, p. 110): $2HCl + O \rightarrow H_2O + 2Cl$, is the result. Then we adjust the equation so that molecular formulæ are used throughout. 2Cl becomes at once Cl_2. The oxygen, however, must also appear as O_2, or a multiple of this, in such equations. Hence the whole equation must be multiplied by 2:

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$

Again, the equation for the preparation of chlorine from potassium permanganate (p. 111) becomes:

$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

Every equation containing an *odd* number of atoms of a substance whose molecules are *diatomic* must be multiplied by 2. Again, mercuric oxide decomposes to give mercury vapor and oxygen (p. 43), and the molecules of mercury are monatomic and those of oxygen diatomic, so we write:

$$2HgO \rightarrow 2Hg + O_2.$$

Finally, the formulæ of substances which are solid or liquid, and cannot be easily vaporized, are written in the simplest terms. Thus, since substances like the copper in the following equation are involatile, the molecular weights of such substances are unknown, and their molecular formulæ likewise: $2Cu + O_2 \rightarrow 2CuO$. Furthermore, in the case of substances which can be volatilized, although the molecular weights and molecular formulæ may therefore be known, we do not usually employ the molecular formulæ if the substance is not used in the form of vapor in the laboratory. Thus, the molecular formula of phosphoric anhydride is P_4O_{10} (p. 132). But we generally make, and use, only the solid form, and not the vapor, in actual work. Hence the action with water is usually written as we have given it (p. 51), rather than in the form: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$.

The applications of the properties of **molecular equations (which will be used exclusively hereafter)** may now be illustrated in detail.

Applications: To Arithmetical Problems. — 1. When a problem in regard to **weights** of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (p. 43).

2. When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and volumes are to be inserted. Note, however, that only the volumes of the substances *in the gaseous condition* are considered.

For example, what volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as shown above (p. 142), together with the full interpretation, are as follows:

$$\begin{array}{lccccc} & 2KClO_3 & \rightarrow & 2KCl & + & 3O_2. \\ \text{WEIGHTS:} & \underbrace{2\,(39.15 + 35.45 + 48)}_{245.2\text{ g.}} & & \underbrace{2\,(39.15 + 35.45)}_{149.2\text{ g.}} & & \underbrace{3 \times 32}_{96\text{ g.}} \\ \text{VOLUMES:} & & & & & 3 \times 22.4\text{ l.} \end{array}$$

(Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which are melted, *but not vaporized* during this, or any action in which we employ them.) Now, as to the problem in hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these* points is that 245.2 g. of potassium chlorate give 67.2 liters (observe that the *coefficients* are used, as well as the molecular weights, in these numbers) of oxygen at 0° and 760 mm., and the question is, What volume will 60 g. give? By proportion, 245.2 g. : 67.2 l. : : 60 g. : x l., where x = 16.4 liters. If a different temperature and pressure had been specified, either the volume in the equation, or the answer, would have had to be converted by rule to the given conditions. It saves time not to write out, as above, the whole interpretation, but only the parts required. For example, if the question is: What volume of chlorine is needed to give 25 g. of aluminium chloride, we may, if we choose, omit all the data excepting the volume of the chlorine and the weight of the aluminium chloride, thus:

$$\begin{array}{ccccc} 2Al & + & 3Cl_2 & \rightarrow & 2AlCl_3 \\ & & 3 \times 22.4\text{ l.} & & 2 \times 133.45\text{ g.} \end{array}$$

The volume of chlorine required is $25 \times 3 \times 22.4 \div (2 \times 133.45)$ liters. These illustrations show the method of calculating actual volumes (see Exercises 8, 9).

3. If the question concerns **relative volumes** only, then it is simplest to use the interpretation of the equation in terms of molecules. For example, What relative volumes of hydrogen chloride and oxygen are required in Deacon's process? The molecular equation is (p. 142):

$$\begin{array}{lccccccc} & 4HCl & + & O_2 & \rightarrow & 2H_2O & + & 2Cl_2. \\ \text{MOLECULES:} & 4 & & 1 & & 2 & & 2 \end{array}$$

Since equal numbers of molecules of gases occupy equal volumes, the proportion 4 molecules of hydrogen chloride to 1 molecule of oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4

molecules of hydrogen chloride give 2 molecules of chlorine, so that the ratio of these substances by volume is 4 : 2, or 2 : 1.

In regard to the water, since that is not a gas at common temperatures, the question, if asked, must be more specific: What are the relative volumes of *steam* and chlorine in the product, as commonly delivered by the action at 400°? It is 2 : 2, or 1 : 1. What are the relative volumes of water and chlorine, after the products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume.*

What is the total volume-change in the foregoing action above 100°? It is a change from 5 molecules to 4. The volume changes in the same ratio. But at 0° the volume-change is from 5 volumes to 2, for the water does not appreciably add to the volume of the products (see Exercises 10, 12).

4. When we know the molecular formulæ of the single substances concerned in an action, the equation can be made, and **the relative volumes determined, without actual measurement.** For example: What volume-change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O_2, and CO_2. The equation representing the weights is $CO + O \rightarrow CO_2$. The molecule of oxygen, however, being O_2, we cannot employ less than this quantity in a molecular equation, so that the equation becomes:

$$2CO + O_2 \rightarrow 2CO_2.$$

Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation (see Exercises 11, 12).

* Of course if an exact answer *must* be given, it can be given. But for this we require the weight and specific gravity of the product. Thus, $2H_2O$ represents 2×18 g. of water. The sp. gr. of water is 1. Therefore the volume of water formed is 36 c.c. The volume of $2Cl_2$ is 2×22.4, or 44.8 liters at 0°. The ratio of water to chlorine by volume at 0° is therefore 36 : 44,800. But, as a rule, we simply give the volumes of solids and liquids as *zero*, compared with those of the gases concerned in the same action.

5. Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many purposes, it is unnecessary to burden our minds with other data in regard to the relative weights of gases. Is hydrogen chloride (HCl) heavier or lighter than carbon dioxide (CO_2)? These formulæ represent the weights of equal volumes (22.4 l.), namely 36.45 g. and 44 g., respectively. Hence the former gas is a little lighter. Remembering that the G.M.V. of air weighs 28.955 g., we can compare the weight of any gas with that of air in the same way.

What are the relative weights of acetylene (C_2H_2, p. 132) and sulphur dioxide (SO_2) as compared with air? The G.M.V. cube holds formula-weights of the first two, namely 26 g. and 64 g., and 28.955 g. of air. Hence acetylene is a little lighter than air, and sulphur dioxide more than twice as heavy (see Exercise 13).

Applications: To Cases of Dissociation. — Several substances yield smaller values for their densities, and therefore molecular weights, when the densities are measured at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, phosphorus pentachloride PCl_5, although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be 31 + 177.25 = 208.25. The density actually observed at 300° gives by calculation not much more than half this value. The direct inference from this is, that the molecules have only half the (average) weight that we expected: or, in other words, are twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it is a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density thus tells us that dissociation has taken place. From the value of the density at various temperatures, we may even calculate the proportion of the whole material which is dissociated. At 300° it is 97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent. Thus, when the temperature is lowered, progressive recombination takes place and the proportion dissociated

becomes less. Finally the vapor condenses and yields the original solid.

Again, sulphur boils at 445°, but can be vaporized at a temperature as low as 193°, under very low pressure. At this temperature the density of the vapor gives the molecular weight 256 ($= 8 \times 32$), and the molecular formula S_8. That is to say, the G.M.V. holds 256 g. of the vapor at 193°. At 800°, however, the density is only one-fourth as great, and the G.M.V. holds only 64 g. (S_2). This means that 256 g. now occupy four times as large a volume as before, *and the increase is additional to the effect of the mere thermal expansion*, which is allowed for in the calculation and eliminated. Hence the molecules have dissociated. At 1700° the molecular formula is still S_2, so that this represents the limit of dissociation: $S_8 \rightleftarrows 4S_2$. When the vapor is cooled, the density increases once more and at 193° recovers completely the greater value. Similar observations show that phosphorus vapor at 313° is all P_4, but at 1700° half of it has dissociated into P_2. Iodine vapor, up to 445°, is all I_2. Beyond this temperature the density diminishes, and when 1700° is reached the vapor is all I. Thus the molecules are diatomic at low temperatures and monatomic at high ones. The densities of oxygen, hydrogen, and chlorine are not measurably affected by heating to 1700°, so that their diatomic molecules exist from temperatures far below 0° up to 1700°, and are evidently very stable.

Applications: Finding the Atomic Weight of a New Element.—By way of reviewing the principles explained in the chapter, let us apply them to the imaginary case of a newly discovered element. The bromide of the element is found to be easy of preparation and to be volatile. The bromide contains 30 per cent of the element, and its vapor density referred to air is 11.8. The analysis can always be made much more accurately than the measurement of vapor density, so that the former number is more trustworthy than the latter.

To find the equivalent of the element, that is, the amount combined with 80 parts (the equivalent) of bromine, we have the proportion $70 : 30 :: 80 : x$, from which $x = 34.3$. The atomic weight must be this, or some small multiple of it.

The G.M.V. of air weighs 28.955 g. (p. 126). Hence the same volume of the vapor of this bromide, which is 11.8 times as heavy as

air, will weigh 28.955 × 11.8, or 341.67 g. This is therefore the molar weight of the compound.

Now 30 per cent of this is the new element:

$$341.67 \times 30 \div 100 = 102.5.$$

Three times the equivalent weight is the multiple nearest to this number, $3 \times 34.3 = 102.9$, the difference being due to error in determining the density. So long as no other volatile compound is known, we adopt this as the atomic weight. The rest of the molar weight (240 parts) is bromine. Thus the formula of the compound is $ElBr_3$, and from this we see that the element is *trivalent.*

In case no volatile compound of the element can be formed, the equivalent is measured as before. Then some of the free simple substance is made, say by electrolysis, and its specific heat is determined. The sp. ht. is about 0.063. Application of Dulong and Petit's law then gives the atomic weight. The product 34.3×0.063 is equal to 2.161. Hence, the equivalent must be multiplied by 3 to give the atomic weight, for this raises the product to 6.48, which is within the limits. Thus the value of the atomic weight is 102.9, as before.

Replies to Questions about Difficulties. — The beginner always becomes confused over one or more of the points raised by the following questions:

Why was 32 g. of oxygen taken as the standard for molecular weights, rather than 16 g.? Read p. 132 and footnote to p. 131.

If O_2 is the smallest mass of oxygen, why do we have formulæ like H_2O and HClO? O_2 is the smallest mass of *free* oxygen, but in combination half as much occurs in many molecules. Read pp. 132, 137, and 138.

Why is not the atomic weight of an element ascertained by simply measuring the density of the elementary substance? Read pp. 139 and 147.

Can we not deduce the valence of an element from knowing the number of atoms in its molecules, and *vice versa?* Some molecular formulæ and valences are: H_2^{I}, O_2^{II}, Cl_2^{I}, Zn^{II}, also Hg (univalent and bivalent), P_4 (trivalent and quinquivalent) and S_8 (bivalent and sexivalent). There is no relation, either observable or to be expected.

Do the molecular weights, oxygen = 32 and hydrogen = 2 mean that the molecules of oxygen are *larger* than are those of hydrogen? This is the ratio of their weights, but none of the phenomena discussed in this chapter are influenced appreciably by their relative sizes, and therefore none of them give any information on the subject. Read the footnote to p. 129.

Exercises. — 1. The weight of 1 l. of a gas at 0° and 760 mm. is 5.236 g. What is the density referred to air and to hydrogen, and what is the molecular weight (pp. 126, 129)?

2. The density of a gas, referred to air, is 6.7. What is the weight of 1 l. (p. 126), and what is the molecular weight (p. 147)?

3. The molecular weight of a substance is 65. What is the density referred to air, and what is the weight of 1 l.?

4. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element, so far as investigation of this one substance can give it (p. 130)? What is its valence?

5. If the molecular weight of oxygen were taken as 100, what would be the volume of the G.M.V. (p. 126)? What would be the molecular weight of water, and what would be the atomic weights of hydrogen and chlorine (pp. 126, 132)?

6. In future nothing but molecular formulæ of free elements must be used (p. 138). Write in molecular form ten of the equations involving gases which are found in the preceding chapters.

7. If a new form of oxygen were found, such that one volume of it required four volumes of hydrogen to produce water, what would be its molecular formula (p. 140)? What would be the weight of 22.4 l.?

8. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of barium peroxide (pp. 46, 143–144)?

9. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into dehydrated rust (Fe_2O_3) (p. 144)?

10. Write out the molecular equations for the interactions of methane and chlorine (pp. 115, 142); and for the burning of phosphorus (vapor) in oxygen (pp. 132, 138, 145). Deduce the volume relations of the initial substances, and of the products, at various temperatures in each case.

11. Write out the molecular equations for the interactions of acetylene and oxygen (p. 145), and of alcohol vapor (b.-p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case.

12. The molecular weight of cyanogen is 52.08. What is its density referred to air, and what the weight of 1 l. at 0° and 760 mm.? It contains 46.08 per cent carbon and 53.92 per cent nitrogen. What is the formula of the substance (p. 41)? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction (p. 145)?

13. What are the relative weights of equal volumes of hydrogen sulphide (H_2S), and hydrogen iodide (HI), compared with air (p. 145)?

CHAPTER XIII

THE ATOMIC HYPOTHESIS

To determine the nature of chemical phenomena requires, as we have found, very elaborate experimentation. And this has to be followed by still more elaborate reasoning before a systematic statement of the precise nature of the change can be made. Yet, when all this has been done, we are still unable to form a clear conception of what manner of procedure the change follows, for the *details* are entirely inaccessible to observation. We should like to know precisely how chemical union is consummated, and how chemical exchange is carried out. We should like to account for the fact that the automatically adjusted proportions of the materials used in every chemical change are entirely uninfluenced by temperature and other conditions. Above all, we should like to know, if possible, what state of affairs determines the employment of an individual unit weight by each element in all its combinations. None of these questions can be answered, however, because nothing can be seen which suggests any answer.

As usual in cases of this kind we construct an imaginary mechanism, a formulative **hypothesis** (p. 86) to account for the facts. In doing so, we are not under the illusion that we are discovering the actual machinery. We realize that we are simply making a sort of diagram which will assist our thought about the thing itself. Now a slight addition to the molecular hypothesis readily furnishes precisely what we need.

Atomic Hypothesis. — According to the molecular hypothesis, all matter is made up of small discrete particles, each of which has the same composition as has the body as a whole. It is difficult, therefore, to avoid the conception that the different materials in each compound molecule are more or less distinct entities also. Hence we make this the basis of a new hypothesis, and attribute to these constituent parts of molecules the properties of the chemical unit

weights which are closely related to them. Thus, these parts must move from one state of combination to another *without alteration in their mass.* Each kind must be composed of a *distinct variety of matter.*

These parts of molecules which we thus suppose to be permanent, coherent masses, are named **atoms.** This word signifies bodies which are not disintegrated (Gk. ἄτομος, uncut, *i.e.* not cut). The relative weights of these imaginary masses are the **atomic weights.**

It should be noted that although atoms, like molecules, are fictions, the atomic weights, since they are measured by experimental methods, are real. They originally received this name when Dalton, an English schoolmaster of Manchester, succeeded in unraveling the complications of the chemical composition of substances by the help of this very hypothesis, and realized for the first time (1802) that the possession by all elements of individual chemical unit weights lay at the basis of the whole system.

We may sum up all that the facts require us to assume about atoms by saying: **Atoms are the units of which molecules are aggregates. Those of like kind have equal masses, and differ from those of other kinds both in mass and the kind of material of which they are made.** The fundamentally different kinds of materials are the chemical elements.

We must carefully avoid, for the present, the introduction of unnecessary complications by inventing for atoms any other properties, such as size, shape, or color, gratuitously. It is to be noted, particularly, that there are no facts in chemistry which require us to suppose that atoms are *incapable of disintegration.* The molecule of oxygen, for example, might be a cluster of particles. Certain facts (p. 140) require us to suppose that this cluster is divisible into *two* parts, but for chemical purposes the half cluster, with relative weight 16, is as small a subdivision as we need. So we take the half molecule as the chemical unit quantity, without inquiring further into its structure. It would only occasion the risk of conflict with facts still to be discovered if we elaborated our fiction any further than is absolutely necessary. Indeed, the phenomena of radioactivity have already compelled us to suppose that there are particles much smaller than atoms (see Radium). Without this assumption the new facts cannot be accounted for in harmony with the molecular hypothesis.

The Atomic Hypothesis and Chemical Change. — The change from chemical units to atoms is so slight that the application of this hypothesis to the description of chemical phenomena is very readily made. The description gains in concreteness, however, from the change. Thus, we consider iron from every source to be made of minute portions of iron matter which are all alike in weight, and presumably also in their other properties. Similarly, all specimens of sulphur are made of minute particles of sulphur having exactly the same weight. The weight of a sulphur atom, however, is different from that of an iron atom. When visible portions of the two substances unite, we conceive the operation to consist in the union of each atom of iron with one atom of sulphur to produce a molecule of ferrous sulphide. The consummation of this union between multitudes of pairs of the respective kinds of atoms in every second of time results in a chemical transformation whose progress is perceptible by the senses.

In more complex chemical changes, a further correspondence between the hypothesis and the facts comes to our notice. For example, when sulphuric acid acts upon sodium chloride to produce hydrogen chloride:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4,$$

one part by weight of hydrogen takes the place of 23 parts by weight of sodium, and combines with 35.45 parts of chlorine to form the hydrogen chloride. This is the way we state the change when we refer to measurable quantities. According to this hypothesis, the operation consists in the repetition, millions of times over within a small amount of material, of the substitution of one atom of hydrogen for one atom of sodium to form a molecule of hydrogen chloride. The special fact which we notice is that the atom of hydrogen suffices exactly to occupy the place of the atom of sodium. If it were somewhat too heavy or somewhat too light, then a single unit weight for hydrogen would not describe the proportions of the element in all its combinations, a situation which would be contrary to the fact recorded in the law of combining weights (p. 34). The remarkable fact about this, and all other double decompositions of the same sort, is that the little masses of the various elements exchange places, without any alterations to fit the new compound being required. Hence our assumption that the atoms are permanent, coherent

wholes. This, of course, is simply stating in terms of the atomic hypothesis the facts which underlie the conception of unit weights. **A chemical phenomenon as we observe it, then, is imagined to consist in some systematic liberation, combination, or exchange of atoms, according to a definite scheme, and repeated many millions of times (once with each molecule) in a body or mixture of bodies.**

The Atomic Hypothesis and the Quantitative Laws.—The idea of atoms simply crystallizes somewhat more definitely the conception of chemical unit weights. Hence, it follows of necessity that the quantitative laws of chemical combination, out of which the latter arose, will be found to be entirely in harmony with the atomic hypothesis. The definite composition of each compound, for example, corresponds to the hypothesis that each substance is made up of a specific kind of molecules, all of which, in turn, contain the same kind and number of atoms.

The conception of valence (p. 70) suggests, in terms of this hypothesis, that some atoms unite with but *one* other atom, habitually (NaCl). Some, however, unite with two of the first kind ($ZnCl_2$), or with one other of their own kind (ZnO), still others with three atoms of the first kind ($AlCl_3$), and so forth. In other words, it involves the assumption that each kind of atom has a limited capacity for holding other atoms in combination. Thus, taking the most crudely mechanical view of the matter, we might elaborate the hypothesis by suggesting that there is a limit to the number of points at which atoms may be attached to one another. When one atom of chlorine is attached to one of sodium, the combining capacity of each is exhausted. When one atom of hydrogen is attached to one atom of oxygen, one combining capacity of the oxygen still remains (H—O—), and can be satisfied by one more atom of hydrogen or of some other element.

Equations and the Atomic Hypothesis.—Since equations are simply *records* of the kinds and quantities of matter taking part in chemical changes, they require no addition to the atomic hypothesis. The symbols, which originally represented unit weights of the various elements, may stand equally well for atoms. Hence, in the current language of chemistry, potassium chlorate ($KClO_3$) is composed of one atom each of potassium and of chlorine, and three atoms

of oxygen, in each molecule. The word "atom" stands for unit weight, and the word "molecule" for molecular weight.

Concretely, when these terms are used, the chemical equation represents one minute specimen of the change which is taking place throughout the whole mass. It shows enough molecules and atoms to furnish a complete example of what, repeated millions of times, will constitute a chemical change in a visible amount of material. There are a few details which this point of view suggests. For example, the equation $HgO \rightarrow Hg + O$ shows the weights, but does not include a complete sample of the materials in the point of view of this hypothesis. The smallest fragment of free oxygen which we can obtain is made of two atoms. Hence two molecules of mercuric oxide are required to furnish them. Thus the minimum number of *molecules* which would suffice for carrying out this change on a molecular scale is $2HgO \rightarrow 2Hg + O_2$. Similarly, since the smallest discrete portions of free hydrogen and chlorine contain two atoms each, we must write the equation $H_2 + Cl_2 \rightarrow 2HCl$ (p. 140).

May other Properties, Besides Definite Mass and Specific Material, be attributed to an Atom? — In one direction, namely, that of accounting for the properties of compounds, no attempt has been made to adapt the atomic hypothesis so as to explain the facts. Thus, two hydrogen atoms in a molecule give a gas almost insoluble in water; two chlorine atoms, a gas which is moderately soluble; but one of each gives hydrogen chloride, which dissolves in water in extraordinary quantities. So also, colorless substances give, by chemical union, strongly colored ones, and odorless substances, by chemical union, strongly odorous ones. Putting pieces of iron and sulphur side by side causes absolutely no change in the properties of either. And yet this hypothesis compels us to assume that if the particles are made fine enough, and placed close enough to one another, the individual properties of the constituents will entirely disappear. Hitherto we have failed to think of any qualities which might be attributed to the atoms in order to account for facts of this class. Why should oxygen (O_2) and ozone (O_3) be so different in behavior, although the atomic theory hints at nothing but a substitution of three atoms for two? What atomic properties shall account for the difference between red and yellow phosphorus? Usually, in explaining these matters, we forsake atoms and employ

the conception of energy. We say that ozone has more energy than oxygen, and yellow phosphorus more than red phosphorus.

There are certain facts, however, such as the chemical actions known as internal rearrangements (p. 10), which are successfully explained by supposing that the atoms composing a given kind of molecule **are disposed towards one another in a definite geometrical arrangement.** We speak then of the **structure** of the molecule and the **constitution** of the substance, and, to represent our conclusions, we use **graphic formulæ** (*q.v.*).

Summing this up, we find that all the suppositions the chemist makes are: That an atom has a specific mass, which is not altered in ordinary chemical change, and consists of a specific kind of material; that its capacity for combining with other atoms is limited by its valence, and, sometimes, that the atoms in a molecule are arranged with reference to one another in space in some definite way. After making this formulative hypothesis, however, he *knows* no more than he did before about the *real* mechanism of chemical change.

Exercises. — 1. In previous chapters our definitions have been *experimental;* that is, have been expressed in terms of facts learned by experiment. In imitation of the definitions of the law of definite proportions and of valence outlined on p. 154, write out theoretical definitions of the following, in terms of the atomic hypothesis: Physical and chemical phenomenon, multiple proportions, chemical unit weight, molecular weight, element, compound, symbol, formula, equation.

2. Criticize the definitions: The atomic weight of an element is the smallest portion of that element which takes part in chemical change. An atom is the smallest particle that can be conceived.

3. Define all the varieties of chemical change (p. 124) in terms of the atomic hypothesis.

CHAPTER XIV

THE HALOGEN FAMILY

THE elements to which we have so far devoted most attention have been oxygen, hydrogen, and chlorine. If we recall the chemical properties and relations of these elements we shall recognize the fact that they all possess very distinct individualities.

The Chemical Relations of Elements. — Hydrogen is the substance (p. 74) which unites readily with oxygen and chlorine, less readily with other non-metals, and scarcely at all with metals. Oxygen and chlorine resemble one another somewhat in the greatness of their chemical activity and the variety of free elements with which they are capable of uniting, but differ markedly in what we have called their chemical relations (p. 116). The resulting compounds belong, in fact, to quite different classes — oxygen forms oxides, chlorine forms chlorides — **and elements are considered similar only when they resemble one another in chemical relations, and produce, by combination with the same element, compounds having similar chemical properties.** Thus the common oxide of hydrogen, water, is a neutral substance, and is chemically rather indifferent. The chloride of hydrogen in aqueous solution is a strong acid and is chemically very active.* If all the other chemical elements differed from one another as much as do these three, they would be incapable of classification. In reality, however, we find that the elements can be grouped together in sets. They are classified according to the kind of substances with which they combine and the chemical nature of the products. In some families the resemblance is close, in others less close. The present group is of the former class, and will serve,

* The difference between oxides and chlorides is seen in their behavior, and will show itself as we proceed. We have already learned, however, that oxides often unite with water to form acids or bases (p. 81). Chlorides do not unite with water to form new substances with marked characteristics (*cf.* p. 83). They belong to the large class of compounds designated **salts** (*q.v.*).

therefore, as a convenient beginning in the work of tracing relations between the elements and in classifying the facts of descriptive chemistry.

The Chemical Relations of the Halogens. — The bromide (NaBr), iodide (NaI), and, to a less extent, the fluoride (NaF), of sodium, resemble sodium chloride (NaCl) in appearance and behavior. From the fact that chlorine, bromine, iodine, and fluorine are thus all able to produce substances which, both in composition and chemical behavior (see p. 187), resemble salt, they are known as the **halogens** (Gk. ἅλς, salt; γεννᾶν, to produce), and their compounds are named the **halides**. The halogens, as the above formulæ show, are univalent. They all form compounds with hydrogen, and these compounds closely resemble hydrogen chloride (*q.v.*). For example, they are colorless, they are gases (except hydrogen fluoride, a very volatile liquid), they are very soluble in water, and their solutions are acids. Other relations will be given in a summary at the end of the chapter.

Bromine Br_2.

Occurrence. — The compounds of chlorine, bromine, and iodine usually occur together in nature, while the compounds of fluorine are not found in the same sources. Bromine occurs chiefly in the form of the bromides of sodium and magnesium, in the upper layers of the natural beds of rock salt.

Preparation. — In the chemical point of view there are three distinct ways in which bromine is made. 1. The first of these is closely related to the common method of preparing chlorine (p. 112). As hydrobromic acid, unlike hydrochloric acid, is not formed extensively in connection with any chemical industry, potassium bromide, the most accessible compound of bromine, is treated with concentrated sulphuric acid, and the product is oxidized with powdered manganese dioxide in one operation. The whole action may be represented in a single equation (see next section), as follows:

$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow MnSO_4 + 2KHSO_4 + 2H_2O + Br_2.$$

Bromine being a volatile liquid, while the two sulphates are involatile, its vapor passes off along with a little water when the above mixture is heated. It is condensed in a worm-tube surrounded by cold water.

2. The second method of preparing bromine depends on the fact that chlorine is a more active element and displaces bromine from combination. When, therefore, chlorine is passed into a solution of potassium or sodium bromide, potassium or sodium chloride is formed and the bromine liberated:

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2.$$

When the liquid is warmed, the bromine passes off along with a part of the water, and may be condensed as before.

3. Aqueous solutions of soluble bromides may be decomposed by means of a current of electricity. The bromine is set free at the positive electrode.

The whole of the bromine used in commerce is at present manufactured in the first two of these ways. Two-thirds of the supply is obtained from Stassfurt, where, after the extraction of the potassium chloride from the impure carnallite ($KCl, MgCl_2, 6H_2O$), the mother-liquor is found to contain the more soluble sodium and magnesium bromides in considerable quantities. The warm mother-liquor trickles down over round stones in a tower. The chlorine is introduced from below and dissolves in the liquid. The bromine is thus liberated and passes off as vapor. A part of our supply of bromine is obtained from the brines of Ohio, West Virginia, and Kentucky. Here the liquid, after most of the common salt has been removed by crystallization, is assayed to ascertain the quantity of bromine which it contains, and is treated with the calculated amount of sulphuric acid necessary for the action. Manganese dioxide is then added in small quantities at a time. In Michigan the brines are treated with electrolytic chlorine. The quantity produced in America in 1906, was 640 tons, and was valued at $165,204.

Partial Equations, a Plan for Making Complex Equations. —When an equation involves more than two initial substances or products, as does the one given above for the first method of preparing bromine, it cannot readily be worked out by the method formerly recommended (p. 41). After the formulæ of all the substances, on both sides, have been set down, it is difficult to hit upon the proper coefficients required to balance the equation. In such cases, a good plan is to select *two* of the initial substances, and make a **partial equation** showing part of the action and including at least one actual product. Any unused units (not constituting a product)

are then set down also and treated as a balance. Thus the first two of the substances, in the above equation, will furnish the second of the products:

$$KBr + H_2SO_4 \rightarrow KHSO_4\ (+\ HBr). \qquad (1)$$

Then we may represent the formation of the first of the products from the materials which evidently must have been used up in forming it, and set down the balance as before:

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O\ (+\ O). \qquad (2)$$

We then perceive that the last of the products might come from the oxidation of the first balance by the second:

$$(2HBr) + (O) \rightarrow H_2O + Br_2. \qquad (3)$$

The third partial equation shows that 2HBr will be needed for the amount of O obtainable from MnO_2, so we go back to (1) and multiply it by two throughout:

$$\begin{array}{rcl} 2KBr + 2H_2SO_4 & \rightarrow & 2KHSO_4\ (+\ 2HBr) \qquad (1) \\ MnO_2 + H_2SO_4 & \rightarrow & MnSO_4 + H_2O\ (+\ O) \qquad (2) \\ (2HBr) + (O) & \rightarrow & H_2O + Br_2 \qquad (3) \\ \hline 2KBr + 3H_2SO_4 + MnO_2 & \rightarrow & 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \end{array}$$

When we now add the real substances used and produced, as they occur in these partial equations, and leave out the balances, which have been adjusted so as to cancel one another, we obtain the final equation already given for the action. It must be observed that this subdivision of the action into parts is a purely arithmetical device. The partial equations made for purposes like the present one are often purely fictitious. It is still true, however, that we are aided in the selection of partial actions at each step by following some plausible theory as to stages for the action which, if there were any, would be chemically conceivable.

Physical Properties.— Bromine is a dark-red liquid (sp. gr. 3.18). It boils at 59°, forming a deep-red vapor, and even at ordinary temperatures gives a high vapor pressure (150 mm. at 18°) and evaporates quickly. When cooled it forms red, needle-shaped crystals (m.-p. 7.3°). A saturated aqueous solution (bromine-water) at ordinary temperatures contains about three parts of bromine in one hundred of water. The element is much more soluble in carbon

bisulphide, alcohol, and other organic solvents. Its vapor density up to 750° is 160 (oxygen = 32).

Bromine (Gk. βρῶμος, a stench) has a most pungent odor. It has a very irritating effect on the mucous membrane of the nostrils and throat. If spilled upon the hands it has a most destructive action upon the tissues.

When free bromine is added to starch emulsion no special change in tint is observable unless a very large amount of the element is used (see Iodine).

Chemical Properties.—The molecular weight of bromine being 160, and the atomic weight 79.96, the molecules of the vapor are diatomic and the molecular formula of the elementary substance is Br_2.

Bromine unites directly with hydrogen. The mixture of the gases is not explosive, and the union is much slower than in the case of chlorine. In presence of finely divided platinum the speed of the action may be considerably increased.

Bromine forms compounds directly, both with non-metals, like phosphorus and arsenic, and with most of the metals. Towards unsaturated substances and organic compounds it behaves like chlorine (*q.v.*). In all cases the interaction is less violent than when chlorine is used, and the element is displaced from combination with hydrogen and with the metals by free chlorine.

Potassium bromide is employed in making photographic plates and in medicine and in the preparation of organic dyes.

Hydrogen Bromide HBr.

Preparation.—It might be expected that the most convenient way of producing this compound would be similar to that used in preparing hydrogen chloride, namely, by the action of concentrated sulphuric acid upon some common bromide, such as potassium bromide ($KBr + H_2SO_4 \rightleftarrows HBr + KHSO_4$). Hydrogen bromide being less stable, however, a large part of it is oxidized by the sulphuric acid and the product is mixed with sulphur dioxide and free bromine.

Since all acids decompose all salts more or less, use of an acid which does not give up its oxygen so readily, such as phosphoric acid, will yield pure hydrogen bromide ($KBr + H_3PO_4 \rightarrow HBr\uparrow + KH_2PO_4$). The small solubility of the salt in concentrated phosphoric acid

retards the interaction and makes the evolution of the gas very slow, however.

Pure hydrogen bromide is best prepared by the action of water upon phosphorus tribromide (see Hydrolysis, below). When bromine and phosphorus are mixed, a violent union of the two elements takes place, producing phosphorus tribromide (PBr_3). This substance, which is a colorless liquid, is in turn broken up with great ease by water, producing phosphorous acid, which is not volatile, and hydrogen bromide:

$$P\begin{matrix} \diagup Br \\ - Br \\ \diagdown Br \end{matrix} + \begin{matrix} HOH \\ HOH \\ HOH \end{matrix} \rightarrow P(OH)_3 + 3HBr.$$

In practice, those two actions are carried on simultaneously. To diminish the vigor of the interaction, red phosphorus is taken instead

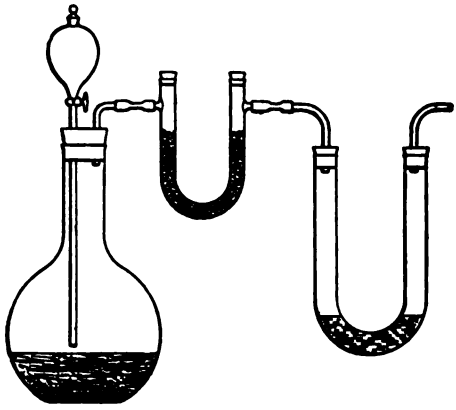


FIG. 47.

of yellow, and is mixed with two or three times its weight of sand in a flask (Fig. 47). A small quantity of water is added. Excess of water must be avoided, as the hydrogen bromide produced is extremely soluble, and would therefore be retained in the flask instead of being disengaged as gas. The bromine is placed in the dropping funnel, and admitted, a little at a time, to the mixture. The gas produced is passed through a U-tube containing glass beads mixed with red phosphorus. The latter combines with any free bromine which may have been carried along with the gas. The

second U-tube, containing water, may be attached when a solution of the gas is required.

Hydrolysis. — The interaction of water with phosphorus tribromide (foregoing section) illustrates an important property of water (p. 81) and a common variety of chemical change. The action is **a double decomposition in which water is one of the interacting substances** and is called **an hydrolysis** (Gk. ὕδωρ, water, and λύσις, the act of loosing). The water divides into the radicals H and OH, and the former unites with the more active non-metal in the substance (as the bromine in PBr_3) and the hydroxyl with the other element. For example, $PCl_3 + 3HOH \rightarrow P(OH)_3 + 3HCl$. All the halides of the non-metals are thus hydrolyzed (see sulphur mono-chloride), as are also some other classes of compounds.

Physical Properties. — Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air. It is easily reduced to the liquid condition. It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to clouds of liquid particles. Pure hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity (see below).

Chemical Properties. — The chemical properties of hydrogen bromide are similar to those of hydrogen chloride (p. 120). It is somewhat less stable, and dissociation into its constituents begins to be noticeable at 800°. When free from water, it is not an acid (see below). The gas interacts vigorously with chlorine, hydrogen chloride and free bromine being produced, $2HBr + Cl_2 \rightarrow 2HCl + Br_2$.

Chemical Properties of Hydrobromic Acid HBr, Aq. — The solution of the hydrogen bromide in water is an active acid (*cf.* p. 75). It conducts electricity extremely well. In contact with certain metals, and with oxides of metals and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 123). In the first case, hydrogen is set free and the bromide of the metal produced. In the other two cases, water and the bromides of the metals are produced. Oxidizing agents set bromine free from hydrobromic acid, and the only difference as compared with hydrochloric acid is that less powerful oxidizing agents can produce this result (p. 161). Chlorine dissolved in water displaces bromine from hydrobromic acid and from soluble bromides with ease.

Iodine I_2.

Occurrence. — Iodine, like bromine, occurs in sea-water, although it is present in much smaller quantities. Fortunately, certain species of sea-weed seem to have the power to remove it from water, and use it as a constituent in complex organic compounds which they contain. In the case of some species, the ash of the sea-weed is said to contain as much as two per cent, or even more. The other chief source of iodine is in Chili saltpeter (mainly $NaNO_3$), in which it is present in the form of small proportions of sodium iodate ($NaIO_3$) and sodium iodide. Of recent years the quantity obtained commercially from this source has greatly increased, while that from sea-weed has diminished.

Preparation. — 1. In factories where the iodine is extracted from sea-weed, the latter is first burned, either roughly in hollows in the ground, or more carefully in specially constructed ovens. A great deal of the iodine seems to be lost by volatilization in this process, but the ash that remains, which is known in Scotland as *kelp* and in Normandy as *varec*, still contains from 0.5 to 1.5 per cent of sodium iodide. The ash is treated with water, and the solution is evaporated so as to permit the deposition of the sodium chloride and sodium sulphate which it contains. The sodium iodide, being very soluble, remains in the mother-liquor. This is then treated with manganese dioxide and sulphuric acid. The quantity of manganese dioxide is carefully measured so as to be just sufficient to set free the iodine contained in the liquid, without proceeding farther to the liberation of the chlorine which it contains in much larger amounts. When the mixture is heated, the iodine passes off in the form of vapor, and is condensed in a suitable receiver. The action (*cf.* pp. 113, 158, 160) is:

$$2NaI + MnO_2 + 3H_2SO_4 \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2.$$

2. In France the treatment is similar, excepting that chlorine is used to liberate the iodine in the last stage ($2NaI + Cl_2 \rightarrow 2NaCl + I_2$). The quantity is adjusted so that excess may not be employed. The iodine, being insoluble, forms a dense precipitate, and, when the liquid is pressed out, it remains behind in the form of a paste.

3. Electricity could also be used for the decomposition of this mother-liquor. The iodine is set free at the positive electrode, while the metals pass to the other.

In all cases the iodine is subjected to purification before being sold. This is carried out by distilling it with a little powdered potassium iodide. It condenses in the solid form directly, in glittering black plates (sublimed iodine). The distillation of a solid body, when a condensation takes place directly to the solid form, is spoken of as **sublimation.**

Physical Properties. — Iodine (Gk. ἰοειδής, like a violet) is a solid substance (sp. gr. 5), exhibiting large crystalline plates of rhombic form. It melts at 114°, and boils at 184°. The vapor has at first a reddish-violet tint, and on being more strongly heated becomes deep blue (see next section).

Iodine is much less soluble in water than are the other halogens, and the solution has a scarcely perceptible brown tint. At ordinary temperatures one part of iodine dissolves in 5000 — 6000 parts of water. It is much more soluble in carbon disulphide (p. 103) and in chloroform, in which it gives violet solutions. In alcohol it gives a solution which is brown. The brown color is attributed to the fact that in alcohol the iodine is in a condition of feeble combination, and not simply in solution. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. In these cases, however, the formation of definite compounds (such as, $KI + I_2 \rightleftarrows KI_3$), by a reversible action, accounts for the amount of iodine which appears to be dissolved.

The behavior of free iodine towards starch forms a distinctive **test** for both substances (*cf.* p. 114). When starch is treated with boiling water it passes into a state of fine suspension, and the liquid may be filtered without removal of all the starch. When traces of iodine, contained, for example, in the pale-brown aqueous solution, are added to this filtered starch emulsion, a deep-blue color is produced. The same action is used as a test for starch. This blue substance is not a chemical compound, but a solution of the iodine in the solid starch which is suspended in the water.

Chemical Properties. — The molecular weight of iodine, ascertained by weighing the vapor at a temperature above the boiling-point, is 254.8. The atomic weight being 126.97, the molecule contains two atoms. This value for the density remains unchanged when the measurement is made at temperatures up to about 700°.

Beyond this point, however, the vapor diminishes in density more rapidly than Charles' law would lead us to expect, and at 1700° the molecular weight has fallen to 127. As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This chemical action is interesting, since it is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable ($2I \rightleftarrows I_2 + 28{,}500$ cal.), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The monatomic and diatomic forms of iodine should be distinct chemical substances, and if the investigation of the behavior of the former were not hampered by the very high temperature at which alone it exists, it would doubtless be found to exhibit different chemical properties.

Iodine forms no hydrate with water. It unites very slowly with hydrogen, even when heated. Iodine unites directly with a number of elements, including some non-metals and the majority of the metals. When phosphorus is presented in the yellow form, the action takes place spontaneously without the assistance of heat. Both chlorine and bromine displace iodine from combination with hydrogen and the metals ($2HI + Br_2 \rightarrow 2HBr + I_2$). The action may be brought about either with the substances in dry form or with their aqueous solutions.

Iodine and its compounds are much used in the arts and medicine. Iodine is applied, in the form of an alcoholic solution (" tincture of iodine "), for the reduction of some swellings. It is required in making iodoform (CHI_3), and the iodides of potassium, rubidium, and sodium, which are used in medicine. Potassium iodide is likewise employed in the manufacture of photographic plates.

Hydrogen Iodide HI.

Preparation. — The direct union of hydrogen and iodine cannot be employed in preparing pure hydrogen iodide. The union takes place slowly at 445°, but, since the action is markedly reversible (*cf.* p. 115), always remains incomplete: $H_2 + I_2 \rightleftarrows 2HI$ (see p. 173).

The action of concentrated sulphuric acid upon potassium or

sodium iodide is equally inapplicable. In this case, as in that of hydrogen bromide (p. 161), the hydrogen halide reduces the sulphuric acid, and much free iodine is formed.

Finely powdered sodium iodide and concentrated phosphoric acid (*cf.* p. 161), when mixed and warmed, give pure hydrogen iodide ($NaI + H_3PO_4 \rightleftarrows HI\uparrow + NaH_2PO_4$). This action, although it goes very slowly, was formerly used in preparing the gas.

The **best method** is one similar to that described under hydrogen bromide. Phosphorus and iodine unite directly to form PI_3. This is a yellow solid which is violently decomposed by water and gives phosphorous acid and hydrogen iodide:

$$PI_3 + 3H_2O \rightarrow P(OH)_3 + 3HI.$$

If excess of water, which dissolves hydrogen iodide, is avoided, the latter goes off in a continuous stream in a gaseous condition.

Still another method of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas (*q.v.*) is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water, I_2 (solid) $\rightleftarrows I_2$ (dslvd), and acts upon the hydrogen sulphide, which likewise dissolves, H_2S (gas) $\rightleftarrows H_2S$ (dslvd). Sulphur separates in a fine powder, S (dslvd) $\rightleftarrows$ S (solid), and hydrogen iodide is formed in accordance with the equation:

$$H_2S + I_2 \rightarrow 2HI + S.$$

This action takes place, however, only in presence of water, although the water does not appear in the equation. The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

Physical Properties. — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128, and it is therefore much heavier than air, the average weight of whose molecules is 28.955 (p. 126). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 0° ten grams of water will absorb ninety grams of the gas, giving a 90 per cent solution. The behavior of this solution is similar to those of hydrogen chloride and hydrogen bromide (*cf.* p. 120). The mixture of constant boiling-point distils over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

Chemical Properties.— Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas, $4HI + O_2 \rightarrow 2H_2O + 2I_2$. When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced, $Cl_2 + 2HI \rightarrow 2HCl + I_2$. Bromine vapor will similarly displace the iodine from hydrogen iodide.

Chemical Properties of Hydriodic Acid HI, Aq. — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acids. With oxidizing agents, for example, such as manganese dioxide, it gives free iodine, just as the others give free chlorine and bromine, respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown ($O_2 + 4HI \rightarrow 2H_2O + 2I_2$).

Although the dry gas is not an acid, the solution has all the ordinary properties of this class of substances (*cf.* pp. 63, 111, 123, 161). The hydrogen may be displaced by metals like zinc and magnesium. The acid interacts with oxides and hydroxides, forming iodides and water.

Fluorine F_2.

The discussion of this element should logically have preceded that of chlorine, since it is, of all the members of the halogen family, the most active. Chlorine was taken up first, however, because its compounds are more familiar. Fluorine is found in combination in nature. It occurs chiefly in the mineral fluorite (calcium fluoride, CaF_2) and in cryolite, a double fluoride of aluminium and sodium ($3NaF, AlF_3$).

Preparation. — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. Until very recently all efforts to isolate the element failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult of separation from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886)

by the decomposition of anhydrous hydrogen fluoride, which is liquid below 19°, by means of electricity. The apparatus (Fig. 48) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature of − 23°. The electrodes are made of an alloy of platinum and iridium, which is the only substance that can resist the action of the fluorine. Hydrogen fluoride, like other hydrogen halides, is a nonconductor of electricity, and a small quantity of potassium fluoride has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative. The U-tube is closed, after the introduction of the hydrogen fluoride, by means of blocks made of calcium fluoride, which is naturally unable further to enter into combination with fluorine. For the reception and examination of the fluorine gas, other copper tubes can be screwed on to the side necks of the apparatus, and, when necessary, small windows of calcium fluoride can be provided. It has been found that fluorine dried with extraordinary precautions is without action on glass.

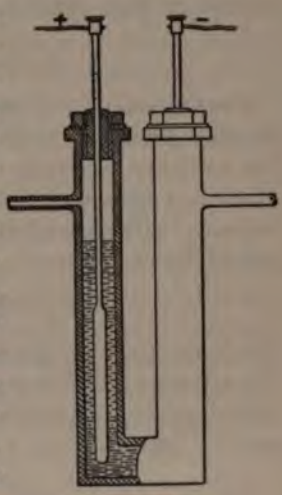


Fig. 48.

Physical Properties. — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density (38) shows that the molecule is diatomic (F_2). The gas is the most difficult of the halogens to liquefy. The liquid boils at − 186°.

Chemical Properties. — Fluorine unites with every element, with the exception of oxygen and the members of the helium family, and in many cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. Fluorine displaces oxygen from water instantaneously

and gives ozone (*q.v.*). On the introduction of a drop of water into a tube of fluorine, the vessel is filled with the deep-blue gas, $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$.

Fluorine displaces the chlorine in hydrogen chloride as easily as chlorine in turn displaces bromine or iodine.

Hydrogen Fluoride H_2F_2.

Preparation. — Pure, dry hydrogen fluoride is best made by heating potassium-hydrogen fluoride, $2KHF_2 \rightleftarrows K_2F_2 + H_2F_2 \uparrow$. For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a platinum retort:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + H_2F_2\uparrow.$$

The hydrofluoric acid passes over and is caught in distilled water. The aqueous solution thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see below).

Physical Properties. — Hydrogen fluoride is a colorless liquid, boiling at 19.4°. It mixes freely with water, and, on distillation, an acid of constant boiling-point (120° at 760 mm.) containing 35 per cent of hydrogen fluoride is obtained. The vapor density of the hydrogen fluoride between its boiling-point (19.4°) and 30° corresponds to a molecular weight of 40, and the formula should therefore be H_2F_2. Above this temperature the vapor becomes gradually lighter (p. 146) and, when 88° is reached, the molecular weight has fallen to 20, corresponding to the formula HF.

Chemical Properties of Hydrofluoric Acid H_2F_2, Aq. — Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen. The action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides. The chief difference in this respect which it exhibits, when compared with the other halogen acids, is one which we should expect from its formula, H_2F_2. We may displace either one or both the hydrogen atoms in the molecule with a metal. Thus, one of the commonest salts of hydrofluoric acid is potassium-hydrogen fluoride

KHF_2 (*q.v.*) mentioned above. In this respect the acid resembles sulphuric acid and other acids containing more than one replaceable hydrogen unit. Salts in which a portion of the acid hydrogen still remains undisplaced are spoken of as **acid salts.**

The most remarkable property of hydrofluoric acid depends on the great tendency which fluorine has to unite with silicon, forming the gaseous silicon tetrafluoride. Glass (*q.v.*) is a mixture of silicates of calcium and sodium, and is rapidly decomposed by hydrofluoric acid. The nature of the change is shown by the two following equations:

$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 + CaF_2 + 3H_2O,$$
$$Na_2SiO_3 + 3H_2F_2 \rightarrow SiF_4 + Na_2F_2 + 3H_2O.$$

All other silicates are decomposed according to the same plan. The silicon tetrafluoride is a gas. The fluorides of calcium and sodium are solid and crumble away or dissolve. Thus the glass is completely disintegrated. The vapor of hydrofluoric acid, generated in the way described above from calcium fluoride in a lead dish, is used for etching glass. The surface of the glass is covered with paraffin to protect it from the action of the vapor, and with a sharp instrument portions of this paraffin are removed where the etching effect is desired. The vapor gives a rough surface where it encounters the glass. The aqueous solution, which may also be employed, makes smooth depressions on the surface.

The Halogens as a Family.

It may be useful here to bring together some of the facts in regard to the halogens and their compounds by way of showing more clearly how far they resemble one another, and in what ways they differ. The most noticeable fact is that, if we **arrange them in order in respect to any one property,** chemical or physical, **the other properties will be found to place them in the same order.** Thus, if we consider (1) the physical properties, we find that the color deepens as we pass from fluorine through chlorine and bromine to iodine. The specific gravities of the elements increase in the same order. The volatility of the elements decreases in the same way — fluorine being the hardest to liquefy, while iodine is a solid and boils at a fairly high temperature. (2) In their chemical behavior, when, for example, they unite with the metals and hydrogen, the vigor of the action is greatest

with fluorine and diminishes progressively until we reach iodine. We shall see later that the affinity for oxygen, on the other hand, *increases* as we pass from fluorine to iodine.

3. The relations of these elements in combination show that they are all univalent in respect to union with hydrogen and metals. In their oxygen compounds (*q.v.*), however, they frequently exhibit a higher valence. The compounds which they form with any one element are usually very similar to one another. All their compounds with hydrogen, for example, become acids when dissolved in water. The oxides interact with water to give acids, and the halogens are therefore non-metals (p. 82). The most noticeable lack of harmony in this group is observed when we consider the solubilities of the corresponding compounds. Thus, the potassium salts are all soluble in water. Silver chloride, bromide, and iodide are almost insoluble, the amount dissolved decreasing in that order. Silver fluoride, however, is quite soluble. Calcium chloride, bromide, and iodide are all very soluble, while calcium fluoride is almost completely insoluble.

It will be noted that the order in which the halogens are thus placed by consideration of most of their properties is the order of increasing atomic weights (see Periodic system).

Compounds of the Halogens with Each Other.

Iodine unites directly with chlorine to form two compounds. The more familiar one is a red crystalline substance, **iodine monochloride** ICl. Another compound, ICl_3, is made by the use of excess of chlorine. Iodine unites with bromine to form the compound IBr, while a compound with fluorine, to which the composition IF_5 has been assigned, is supposed to exist. None of these compounds are particularly stable, and some of them decompose easily.

Exercises. — 1. What impurities is commercial iodine likely to contain? In what way does heating with potassium iodide (p. 165) free it from these?

2. Classify all the chemical actions in this chapter according as they belong to one or other of the ten kinds (pp. 124, 163).

3. What are the relative volumes of the gases in the interaction of chlorine with hydrogen bromide (p. 163), and hydrogen iodide (p. 168), respectively?

4. Tabulate, more fully and specifically than is done in the section on "The Halogens as a Family," (*a*) the physical properties, (*b*) the chemical properties, (*c*) the chemical relations, of the members of this group.

5. Construct the equation on p. 164 by the use of partial equations as in the example on p. 160.

6. What are the relative volumes of fluorine and ozone in the action of the former upon water (p. 170)?

7. What relative volumes of chlorine and iodine vapor must be taken to make the two chlorides of iodine (p. 172), respectively?

CHAPTER XV

CHEMICAL EQUILIBRIUM

In spite of its formidable title, this chapter will introduce nothing novel. Its purpose is to collect together and organize more definitely a number of scattered facts and ideas which have already come up in various connections. On this account, however, it will be all the more necessary for the reader to refresh his remembrance of these facts and ideas by re-reading all pages to which reference may be made.

Reversible Actions. — In discussing the union of hydrogen and iodine at 445° (p. 166), it was indicated that the progress of the action ceases while yet a large amount of *both* the substances necessary for its maintenance still remains available. Now the materials left over are presumably no less capable of uniting than the parts which have already united. The solution of this mystery lies in the fact (p. 168) that *decomposition of the compound* can begin at 180°, and therefore takes place actively at 445°. Hence the product of the union must begin to dissociate, in part at least, as soon as any of it is formed. Thus two changes, one of which undoes the work of the other, must go on simultaneously. In consequence of this, neither can reach completion. At 445°, the system reaches equilibrium when 79 per cent of hydrogen iodide and 21 per cent of the free components are present. As we should expect, experiment shows that it makes no difference whether we start with the elements or with the compound: the proportions of the materials found in the tube, after it has been heated for a sufficient length of time, are in both cases the same. A general statement may be founded on facts like this, to the effect that **a chemical action must remain more or less incomplete when the reverse action also takes place under the same conditions.** Two arrows pointing in opposite directions are used in equations representing reversible changes:* $H_2 + I_2 \rightleftarrows 2HI$, or $2HI \rightleftarrows H_2 + I_2$.

* The reader must avoid the idea that a reversible action is one which goes to completion, and then runs back to a certain extent. This conception would be contrary to the fact, and inexplicable by the kinetic method.

The foregoing example of a reversible action, and the following examples which very closely resemble it, should now be studied attentively in connection with the discussion (for which they furnish the basis) in this and the following sections: (1) The interaction of chlorine and water (p. 115), which was fully discussed at the time; (2) The behavior of phosphorus pentachloride vapor (p. 146); (3) The behavior of water vapor (p. 81), of phosphorus vapor (p. 147), of sulphur vapor (p. 146), and of iodine vapor (p. 166).

When the action is one which is reversible, but, under the circumstances being discussed, proceeds far towards completion in one direction, the arrow will be modified to indicate this fact:

$$Cl_2 + H_2O \leftrightharpoons HCl + HClO \text{ (p. 115).}$$

When this relative completeness is due to precipitation or volatilization, the fact may be indicated by vertical arrows:

$$NaCl + H_2SO_4 \leftrightharpoons NaHSO_4 + HCl\uparrow \text{ (p. 117).}$$
$$NaCl\downarrow + H_2SO_4 \leftrightharpoons NaHSO_4 + HCl \text{ (p. 118).}$$

All chemical actions do not belong to the reversible, incomplete class. Many proceed uninterruptedly to exhaustion of one, or all, of the ingredients. For example, equivalent amounts of magnesium and oxygen combine completely, $2Mg + O_2 \rightarrow 2MgO$. Here, however, the product is not decomposed even at the white heat produced by the vigor of the union. Indeed, magnesium oxide cannot be decomposed, and the action reversed, at any temperature we can command. The other complete actions are so because they are likewise irreversible.

Kinetic Explanation. — Restating these facts in terms of the kinetic hypothesis will enable us to reason more clearly about this variety of chemical change. Suppose we start with the materials represented on one side of such an equation, say the free hydrogen and iodine in that on p. 174. The molecules of these materials will encounter one another frequently in the course of their movements. In a certain proportion of these collisions the chemical change will take place. In the earliest stages there will be few of the new kind of molecules (say of hydrogen iodide), but, as the action goes on, these will increase in quantity. There will be two consequences of this. In the first place the parent materials will diminish in amount, the collisions between their molecules will become fewer, and the

speed of the forward action will therefore become less and less. In the second place the increase in the number of molecules of the products will result in more frequent collisions between them, in more frequent occurrence of the chemical change which they can undergo, and thus in an increase in the speed of the reverse action. The forward action begins at its maximum and decreases in speed progressively; the reverse action begins at zero and increases in speed. Finally the two speeds must become equal, and at that point perceptible change in the condition of the whole must cease.

The most immediate inference from this mode of viewing the matter is, that the apparent halt in the progress of the action does not indicate any cessation of either chemical change. Both changes must go on in consequence of the continued encounters of the proper molecules. But since the two changes proceed with *equal speed* they produce no alteration in the mass as a whole. In fact, the final state is one of equilibrium, and not of rest, one of poise and not of repose. Hence, chemical changes which are reversible lead to that condition of seemingly suspended action which we speak of as **chemical equilibrium**. The changes themselves are called **reversible**, or, since they arrive at a state of balance between opposing tendencies, **balanced actions**.

Chemical Equilibrium and its Characteristics. — The detailed discussion of the relations of liquid and vapor (pp. 78, 90–92), and of saturated solution and undissolved solid (pp. 101, 105–107), has already familiarized us with the term equilibrium and its significance. By the use of the kinetic hypothesis we can, in fact, apply sets of the ideas elaborated in these connections to the discussion of any kind of reversible phenomena.

In particular, the reader will note that the **three characteristics of a state of equilibrium**, developed and illustrated in the case of the physical equilibrium between a liquid and its vapor (p. 91), apply also to a typical case of chemical equilibrium, such as that of hydrogen and iodine before us. Thus:

1. There are **the two opposing tendencies, which ultimately balance one another**. Here they are the tendency of the hydrogen and iodine to produce hydrogen iodide, and the tendency of the hydrogen iodide to reproduce the elements by its decomposition. In other words

they are the **apparent activity** of the hydrogen and iodine interaction, and the **apparent activity** * of the hydrogen iodide decomposition.

2. **At equilibrium the two opposing tendencies or activities are still in full operation,** although their effects then neutralize one another.

3 (and this is the chief mark of chemical, as it is of physical equilibrium). The system is in a sensitive state, so that **a change in the conditions** (temperature and pressure or concentration), even if slight, **produces a corresponding change in the state of the system, and does this by favoring or disfavoring one of the two opposing tendencies or apparent activities.** Such a change is called **a displacement of the equilibrium,** for the system settles down in a new state of equilibrium corresponding to the changed conditions. Thus, in the present instance, a change from 445°, where 79 per cent of the hydrogen and iodine are in combination, to some other temperature, favors one or other of the two opposing actions (according as the new temperature is higher or lower than before), and measurement at the new temperature shows that the proportion of the combined to the free material has altered. The hydrogen iodide equilibrium is affected by changes in concentration also, as we shall presently see (pp. 179, 183).

Now, the foregoing facts show that the key to understanding apparent chemical activities, their magnitudes, their changes, and their practical results, *must lie in knowing how changes in the conditions affect them.* Hence, to the chemist, familiarity with the influence of conditions on chemical phenomena must be of the greatest practical importance. We therefore address ourselves to the discussion of this subject.

The "conditions" to be considered are familiar, — temperature, and concentration or pressure. The "apparent activity of an action" which is affected by these conditions, on the other hand, is a less easily specified thing. But, in cases of equilibrium at least, it is accurately measured by the speed with which the action proceeds. Thus, if the foregoing section be reëxamined, it will be seen that we spoke throughout of the *speed*, rather than of the tendency or activity. So that when we require to consider some-

* We use the term apparent activity for the activity as we see it. In the same action it varies with the conditions. The **intrinsic activity** or **affinity,** on the other hand, is the absolute activity of the action *irrespective of conditions.* Its value can be determined only by eliminating the effect of conditions, a matter which is too abstract for consideration here. The apparent activity is the practical thing which we observe.

thing more definite than the activity we shall use the speed of the action.

Finally, temperature and other conditions influence also the activities in, and therefore the speeds of, those actions which proceed to completion, and are not reversible. Hence, unless our statements are expressly restricted to reversible actions and to states of equilibrium, they apply to all chemical changes.

The Influence of Temperature. — The activity of chemical change, and therefore the speed of all chemical changes, is increased by raising the temperature and diminished by lowering it (*cf.* p. 53). Thus, zinc displaces hydrogen more rapidly from hot than from cold hydrochloric acid. Different actions are affected in different degrees, and no simple rule accurately defining the effect can be given. Roughly speaking, however, a rise of 10° doubles the speed of every action.

In a reversible change the two opposing actions *are different actions* and their speeds are therefore affected in different degrees by the same alteration in temperature. Hence, when the temperature is changed, the relative amount of the two sets of materials present is altered and the equilibrium is displaced. The displacements of the equilibrium by raising or lowering the temperature were mentioned in the description of each of the actions in the reference list in the first section of this chapter. Thus, when phosphorus pentachloride is heated (p. 146), the vapor is a mixture of the pentachloride with the trichloride and free chlorine: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. At 200°, 51.5 per cent of the material is present as pentachloride and 48.5 per cent as trichloride and chlorine. Raising the temperature to 250° changes the proportions to 20 per cent and 80 per cent, respectively. At 300° only 3 per cent of the pentachloride remains. Evidently, here, raising the temperature favors the decomposition of the pentachloride, and therefore increases the speed of its dissociation more than it does the speed of the re-union of the trichloride and chlorine.

The Influence of Concentration. — Leaving, now, the temperature out of consideration, or considering it to be constant, we take up the influence of concentration upon apparent activity. We have seen (p. 175) that the speed of a chemical change is determined by

the frequency with which the molecules of the necessary substances encounter one another. The frequency of the encounters amongst a given set of molecules, resulting in a definite chemical change, will in turn evidently depend entirely upon the degree to which the molecules are concentrated in each other's neighborhood. Larger amounts of one of the materials, for example, will not result in more rapid chemical action, if the larger amount of material is also scattered through a larger space. Chemical changes, therefore, are not accelerated by increasing the mere quantity of any ingredient, but only by increasing the **concentration of its molecules.** Thus, a large amount of hydrochloric acid with a piece of zinc will generate hydrogen no faster than a smaller amount. But substitution of more concentrated acid will instantly increase the speed of the action. In the second case, the number of molecules of the acid reaching the zinc per second is greater, and this action, being non-reversible, proceeds more rapidly to complete consumption of the zinc. With a reversible action the effect on the speed is the same, excepting that the continued activity of the reverse action prevents the direct one from reaching completion. Thus, if, in the action of hydrogen upon iodine, we introduce *into the same space* an extra amount of hydrogen, this facilitates the formation of hydrogen iodide by increasing the possibilities of encounter between hydrogen and iodine. At the same time it does not affect (*cf.* p. 60) the number of encounters in a given time of hydrogen iodide molecules with one another which result in the reverse transformation. The proportion of hydrogen iodide formed, therefore, from a given amount of iodine will be greater, although the total possible (by complete consumption of the materials) has not been altered, since the quantity of one ingredient only has been increased. The introduction of an excess of iodine would have had precisely the same effect.

It is easy to illustrate this experimentally. If ferric chloride and ammonium thiocyanate are mixed in aqueous solution, a liquid containing the soluble, *blood-red* ferric thiocyanate is produced. The compound radicals are (NH_4) and (CNS), and the action is a simple double decomposition:

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl.$$

The action is a reversible one, and the mixture is homogeneous, *i.e.* there is no precipitation. Now, if the two just-named salts are

mixed in very dilute solution in the proportions required by the equation, say by adding 20 c.c. of a decinormal solution (p. 99) of each salt to several liters of water, a pale-reddish solution is obtained. When this is divided into four parts, and one is kept for reference, the addition of a little of a concentrated solution of ferric chloride to one jar, and of ammonium thiocyanate to another, will be found to deepen the color by producing more of the ferric thiocyanate. On the other hand, mixing a few drops of concentrated ammonium chloride solution with the fourth portion will be found to remove the color almost entirely, on account of its influence in accelerating the backward change.

The general principle discussed and illustrated in this section may be called **the law of molecular concentration**, and may be stated as follows: **In every chemical change the apparent activity, and therefore the speed of the action**, at any moment, **is proportional to the molecular concentration** for the time being **of each interacting substance.** This holds whether the action is reversible or not.

We shall next give a more precise, semi-mathematical formulation of this law, as this formulation will be of use later,* and then proceed to illustrate the application of the law, by showing how it explains large classes of actions of which we have already encountered many examples.

***Formulation of the Law of Molecular Concentration.**—The mathematical formulation of the law describing the influence of the concentration of the molecules of each participating substance upon the speed of the action, and therefore upon the apparent activity of the action, is extremely simple. When the actual concentrations of the molecules are specified (in moles (pp. 99, 129) per liter), and the speed is suitably expressed (in moles transformed per minute or per hour), we find that the speed is proportional to the concentration of each molecule appearing in the molecular equation for the action. Thus in the interaction of hydrogen and iodine, if $[H_2]$ and $[I_2]$ represent the concentrations of the molecules H_2 and I_2, and k is a constant, and S is the speed, then:

$$[H_2] \times [I_2] \times k = S.$$

* This mathematical formulation of the law is not required, or referred to in the sections which follow. The section may therefore be omitted for the present and taken up in connection with Chap. xxxiv.

Again, for the dissociation of phosphorus pentachloride vapor into phosphorus trichloride and chlorine (p. 146): $PCl_5 \rightarrow PCl_3 + Cl_2$, if $[PCl_5]$ represent the concentration of the PCl_5 molecules, k_1 is a constant, and S_1 is the speed of decomposition:

$$[PCl_5] \times k_1 = S_1.$$

Similarly, for the reverse action: $PCl_3 + Cl_2 \rightarrow PCl_5$, if $[PCl_3]$ and $[Cl_2]$ stand for the molecular concentrations of these substances:

$$[PCl_3] \times [Cl_2] \times k_2 = S_2.$$

The constant has a different value in each separate action. It includes the value of the intrinsic affinity or activity of the substances, and the catalytic effect (p. 54), if any, of the materials present.

The foregoing plan may be used further to formulate **the condition for chemical equilibrium.** As we have seen (p. 176), a characteristic of a system in chemical equilibrium is that the apparent activities of the opposing actions balance one another, and therefore the speeds of the forward and reverse actions have become equal. If, then, $[PCl_5]_{eqm.}$, $[PCl_3]_{eqm.}$, and $[Cl_2]_{eqm.}$ now represent the molecular concentrations when the system has reached *equilibrium*, then, since the speeds are equal:

$$[PCl_3]_{eqm.} \times [Cl_2]_{eqm.} \times k_2 = [PCl_5]_{eqm.} \times k_1$$

$$\frac{[PCl_3]_{eqm.} \times [Cl_2]_{eqm.}}{[PCl_5]_{eqm.}} = \frac{k_1}{k_2} = \text{constant.}$$

In words, this means that if we change the amount of the pentachloride placed in the vessel, or if we use amounts of chlorine and trichloride which are not equivalent, the numerical value at equilibrium of each concentration ($[PCl_3]$ etc.) will, of course, be different, but the product of the concentrations of trichloride and chlorine, divided by the concentration of the pentachloride, will always give the same numerical value for the constant at the same temperature. This numerical value is called the **equilibrium constant.**

Applications: The Forward Action. Homogeneous and Inhomogeneous Systems. — While there are all degrees of speed in chemical actions, yet in practice we quickly distinguish two different classes. There is a class of actions of which most examples are almost instantaneously accomplished, and a class in which, fre-

quently, the operation takes minutes or even hours. The classes overlap, but, in a general way, the following distinction may be made.

To the former, speedy class belong the explosion of hydrogen and oxygen or other gaseous mixtures, and the interactions when solutions are mixed, as in precipitations. In view of the foregoing explanations, we perceive that the **rapid accomplishment of** such **actions is due,** not so much to any especially great intrinsic affinity, as **to the homogeneous state of mixture of the interacting materials.** This, of course, is a purely physical, and not a chemical motive for speedy interaction. In intimate mixtures, every molecule has an equal opportunity freely to encounter every other molecule and there is therefore no mechanical impediment to the operation of the affinities of the substances. Hence the apparent activity is great.

To the second class, comprising the slower actions, belong cases like the interaction of a piece of zinc with hydrochloric acid, or of manganese dioxide (p. 111) with the same acid, whereby hydrogen and chlorine, respectively, are slowly evolved, and the solid is gradually consumed. Here the hindrance is evidently the fact that the interacting substances are not intimately mixed. **In the slow actions, the system is inhomogeneous.** Pulverizing the solid before use will increase the speed, indeed, but will not transfer the action to the rapid class. It is chiefly the *dissolved* part of the substance which interacts, for chemical action takes place between molecules, and only the dissolved part is disintegrated in such a way that the molecules are readily accessible. Thus, the action is held back by continual waiting for the slow replenishment, from the "insoluble" solid, of the supply of dissolved molecules. In the cases cited, the restraining influence of the dissolving process, which is part of the whole phenomenon, may be formulated thus:

$$Zn(\text{solid}) \rightleftarrows Zn(\text{dslvd}) + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$MnO_2(\text{solid}) \rightleftarrows MnO_2(\text{dslvd}) + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$

Here, again, the mechanical details, depending on physical properties, have more to do with the progress of the action than has the chemical affinity. In terms of the law of concentration, the action is slow, and the apparent activity small, because the concentration of the acting molecules of one of the substances is very small, and cannot be increased because of low solubility (*cf.* p. 162, first line).

Applications: The Reverse Action. Displacement of Equilibria. — We have just seen (p. 179) that one way in which a reversible action may be forced nearer to completion, in one direction or the other, is the introduction of an excess of one of the ingredients contributing to the forward action. This method of displacing the equilibrium point, however, cannot be very effective, unless it is possible to introduce an exceedingly large excess of the selected ingredient in a high degree of molecular concentration, since this operation *does not in any way effect or, in particular, restrain the reverse action* which is continually undoing the work of the forward one. A much more effective **means of furthering the desired direction of such actions is found,** therefore, **in the restraint or practical annulment of the reverse action.** A good way of accomplishing this is to **allow the products of the direct action to separate into an inhomogeneous mixture.** Any agency which could remove the free iodine vapor as fast as it was formed in the decomposition of hydrogen iodide, for example, would entirely stop the reproduction of the compound, and so would enable the dissociation ($2HI \rightarrow H_2 + I_2$) to run to completion.

This might be realized by causing one end of a sealed tube charged with hydrogen and iodine, after the contents had settled down to a condition of equilibrium, to project from the bath in which the whole had been kept at 445° (Fig. 49, which is simply diagrammatic). By cooling this end, a large part of the 21 per cent of free iodine would quickly be condensed in it to the solid form, while the hydrogen would remain gaseous. In other words the concentration of the free iodine would be greatly reduced. In fact, only the trace of vapor which cold iodine gives would then be available to interact with the hydrogen, and reproduce hydrogen iodide. Meanwhile the decomposition of the latter would go on, and thus, eventually, almost all the iodine would be found free in one end of the tube, and the hydrogen, all free likewise, would occupy the rest. By this purely mechanical adjustment the chemical change would therefore be carried from 21 per cent completion to almost absolute completion:

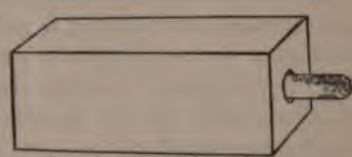


FIG. 49.

$$2HI \leftrightarrows H_2 + I_2(\text{vapor}) \leftrightarrows I_2(\text{solid}).$$

If, on the other hand, arrangements were made to have powdered marble, in a sealed bulb of thin glass, inclosed in the tube, we might imagine the very opposite effect of the above to be produced. The breaking of the bulb of marble, when equilibrium had been reached, would provide means for the removal of all the hydrogen iodide,* while the hydrogen and iodine would still be gaseous. Thus, the compound (HI) having been reduced in concentration to the point of being removed entirely, there would be no reverse action to compensate for the union of the elements. The whole material would, therefore, soon have passed through the form HI. Hence, by another mechanical arrangement, an action which ordinarily could progress to only 79 per cent would be turned into a complete one:

$$H_2 + I_2 \rightleftarrows 2HI \ (+ \ CaCO_3 \rightarrow CaI_2 + H_2O + CO_2).$$

In every-day chemical work, since our object is usually to prepare some one substance, chemists either avoid chemical changes which are notably reversible, or adjust the conditions, as is done in the foregoing illustrations, so that the reverse of the action which they desire is prevented. In consequence of this, when carrying out the directions for making familiar preparations, the fact that such actions are reversible at all very readily escapes our notice. Arranging the conditions so that the separation of a solid body by precipitation, or the liberation of a gas, takes place, are the two commonest ways of rendering a reversible action complete. Excellent examples of both of these are furnished by the chemical change used in producing hydrogen chloride by the inter-action of salt and sulphuric acid, the full discussion of which (p. 118) should now be studied attentively in the light of these explanations (p. 24, footnote).

The reader will find in Brin's process (p. 46), where the concentration of the oxygen is changed by the use of pumps, another exemplification of the principles explained in this chapter. The behavior of hydrates (p. 83) furnishes a whole class of illustrations.

Exercises. — 1. Explain the completeness of the action by which hydrogen chloride and water, respectively, are formed by direct union of the elements.

* The hydrogen iodide would be destroyed by interaction with the marble:

$$2HI + CaCO_3 \rightarrow CaI_2 + CO_2 + H_2O.$$

The calcium iodide is a solid. The two gases, carbon dioxide and water vapor, are here assumed not to interact with hydrogen or with iodine, and would not, therefore, interfere with the formation of fresh hydrogen iodide.

2. Explain the completeness of the action by which silver chloride (p. 8) is formed.

3. Explain why the decomposition of potassium chlorate is complete.

4. In view of the statement on p. 45, explain why mercuric oxide is completely decomposed by heating. Point out the resemblance between this experiment and the imaginary one illustrated in Fig. 49 (p. 183).

5. Why can magnetic oxide of iron be reduced completely by a stream of hydrogen (p. 75), and iron oxidized completely by a current of steam (p. 67)?

6. What actions in Chap. xiv are complete for the same reason that the action of sulphuric acid on salt (pp. 161, 167, 170) is so?

7. With the phosphorus pentachloride system, say at 250°, what effect would suddenly enlarging the space containing a given amount of the vapor produce? What would be the effect of diminishing the space? What would be the effect of introducing additional chlorine into the same space (p. 179)?

8. By what practical means could the degree of dissociation of sulphur vapor (S_8) be reduced, without changing the temperature (p. 146)?

CHAPTER XVI

OXIDES AND OXYGEN ACIDS OF THE HALOGENS

THE chief subjects of practical importance touched upon in this chapter are connected with bleaching powder ($CaCl(OCl)$), and potassium chlorate ($KClO_3$) and perchlorate ($KClO_4$). Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter many actions of a complex and, to us, more or less novel kind.

Compounds of Chlorine Containing Oxygen. — The following are the names and formulæ of the substances:

$HClO$ Hypochlorous acid,	Cl_2O Hypochlorous anhydride,
[$HClO_2$] Chlorous acid,	. . . . .
. . . . .	ClO_2 Chlorine dioxide,
$HClO_3$ Chloric acid,	. . . . .
$HClO_4$ Perchloric acid,	Cl_2O_7 Perchloric anhydride.

There are also compounds of metals with the negative radicals of these acids. Of this nature are the three substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite ($KClO_2$) and some other derivatives have been made.

The two anhydrides (p. 51), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide (*q.v.*), however, is not related to any one acid in this way.

All these compounds differ from most that we have hitherto discussed, inasmuch as not one of them can be made by direct union of the simple substances.

Nomenclature of Acids and Salts. — When several compounds closely related in composition, like the above acids, are known, a systematic method of naming them is used. The terminations *-ous* and *-ic* indicate smaller and larger proportions of oxygen respectively

(*cf.* p. 51). For compounds below or above those two in their degree of oxidation, the prefixes *hypo-* and *per-* are employed.

When the negative radicals (p. 64) of the acids are combined with metals, the compounds are spoken of as **salts** of the respective acids. Thus, $KClO_3$ is described as the potassium salt of chloric acid. The specific names for these salts are distinguished by terminations corresponding to those of the acids:

$KClO$ Potassium hypochlorite,	$HClO$ Hypochlorous acid,
$KClO_2$ Potassium chlorite,	$HClO_2$ Chlorous acid,
$KClO_3$ Potassium chlorate,	$HClO_3$ Chloric acid,
$KClO_4$ Potassium perchlorate.	$HClO_4$ Perchloric acid.

The termination *-ite* corresponds to *-ous*, *-ate* to *-ic*. This principle is applied systematically, so that the salts of sulphuric and sulphurous acids, for example, are called sulphates and sulphites respectively (*cf.* p. 71).

Compounds containing two elements only receive the termination *-ide*. Thus, KCL is potassium chloride, FeS is ferrous sulphide.

Salts and Double Decomposition. — We have just been using the word *salt* in a general sense (*cf.* p. 157). It is the class name for a set of substances which includes common salt or sodium chloride ($NaCl$), potassium nitrate (KNO_3), sodium sulphate (Na_2SO_4), silver chloride ($AgCl$), potassium chlorate ($KClO_3$), etc. The majority of the substances used in elementary chemistry belong to this class. They receive the name because in certain important chemical respects *they behave like common salt.* For example, when sodium chloride was treated with sulphuric acid (p. 117) or phosphoric acid (p. 118), an exchange of radicals took place. An action of the same type was that of sodium chloride and silver nitrate in aqueous solution (p. 8). Here we have two salts interacting, instead of an acid and a salt, and the interchange of radicals is exactly similar:

$$NaCl + H_2(SO_4) \rightleftarrows NaH(SO_4) + HCl\uparrow$$
$$NaCl + AgNO_3 \rightleftarrows NaNO_3 + AgCl\downarrow.$$

Now **salts in general** behave in these respects in the same way as does common salt. They **interact with acids or other salts,** particularly in solution, in such a way that **an exchange of radicals takes place.** In the first case, a salt and an acid, and in the second case two salts,

are produced. **These actions are all reversible.** Acids differ thus from salts only in the fact that one of their radicals is hydrogen. Hence they are frequently called hydrogen chloride, hydrogen sulphate (H_2SO_4), and so forth. It may be added that **bases** (p. 81), like potassium hydroxide (KOH), interact reversibly with salts and acids, exchanging radicals after the same fashion (*e.g.* pp. 123, 189, 191).

All salts are named according to the radicals which they contain. Thus, all containing SO_4 are sulphates. Conversely, when the name of a salt is given, the formula can be written down at once. In doing this, however, regard must be had to the valence of the radicals (p. 70).

In view of the reversibility of most of the interactions of salts, acids, and bases, we encounter completed changes chiefly when precipitation occurs, or when one product is volatile (p. 184). If neither of the products formed by the exchange of radicals is insoluble, the reversibility of the action prevents our obtaining anything but a mixture. Only those double decompositions which involve more or less insoluble or volatile substances are thus of use for preparing salts. The action of sodium chloride on silver nitrate is an example. The silver chloride is almost completely insoluble, while the sodium nitrate produced by the change remains dissolved. By filtration we obtain the silver chloride as a powder, while the evaporation of the filtrate gives us the soluble product. This sort of action can be used, therefore, **either for the preparation of a soluble or an insoluble substance.** If the problem is to make a *soluble* product, then we must arrange an action between two substances, each containing one of the two required radicals, and possessing two other radicals, which, when united, give an insoluble body. This plan is illustrated frequently in what follows (*e.g.* pp. 195, 197).

Preparation and Properties of Hypochlorites. — Since none of the acids in our list can be made directly from their elements, we generally have to prepare, first, the corresponding salt. From the salt, by double decomposition, the acid is then secured. Hence, in each case, the salts will be discussed first.

Chlorine interacts slightly with water (p. 115), producing small quantities of hydrogen chloride and hypochlorous acid (equation (1), below). The action is very strongly reversible. That is to say, since

the last two substances interact very vigorously to reproduce chlorine and water, the direct action does not make much progress.

When, however, some substance which can interact with one or both of these products is added to the solution of chlorine, or when chlorine gas is simply passed into an aqueous solution of such a substance, displacement of the equilibrium point at once occurs (p. 183). Now potassium hydroxide is a suitable substance. It interacts almost completely in solution with both the products of this action, producing potassium chloride (2) and **potassium hypochlorite** KOCl (3), according to the last two of the following equations:

$$Cl_2 + H_2O \leftrightharpoons HCl + HOCl, \quad (1)$$
$$HCl + KOH \rightarrow KCl + H_2O, \quad (2)$$
$$HOCl + KOH \rightarrow KOCl + H_2O.^* \quad (3)$$

Thus, omitting the water, which appears both among products and initial substances and in any case is present in large excess as a solvent, and omitting also the two acids, which are used up as quickly as they are produced by equation (1) and are not amongst the actual products, we get, by addition of the three partial equations (*cf.* p. 159), the final equation:

$$Cl_2 + 2KOH \rightarrow KCl + KOCl + H_2O.$$

This sort of action does not give pure potassium hypochlorite, but for some purposes the presence of potassium chloride in the solution is not objectionable.

Bleaching powder, CaCl(OCl), is manufactured on a large scale by an action exactly like the above. The neutralization* of a molecule of each of the two acids, however, can be accomplished by a *single* molecule of slaked lime (calcium hydroxide, $Ca(OH)_2$), since the latter contains *two* hydroxyl (OH) groups. The lime can be applied, either in the dry form or mixed with some water as a paste. The separate actions and final equation are as follows:

$$Cl_2 + H_2O \leftrightharpoons HCl + HOCl \quad (1)$$
$$Ca\begin{cases} OH + HCl \rightarrow \\ OH + HOCl \rightarrow \end{cases} Ca\begin{cases} Cl \\ OCl \end{cases} + 2H_2O \quad (2)$$
$$\overline{Cl_2 + Ca(OH)_2 \rightarrow CaCl(OCl) + H_2O}$$

* The double decomposition of potassium hydroxide, or any other base, with any acid to produce a salt and water, is called **neutralization** (*cf.* p. 188).

Bleaching powder (*q.v.*) is a salt of calcium involving two different acid radicals (a mixed salt). This condition, again, does not interfere with the application of the substance commercially. A method of obtaining pure hypochlorites, however, will be found below.

Three **chemical properties of hypochlorites** deserve mention: They change into chlorates (*q.v.*) when heated. They may also give off oxygen, $2CaCl(OCl) \rightarrow 2CaCl_2 + O_2$. Although this decomposition is slow in cold solutions of hypochlorites, or when they are preserved in the dry form, it may be hastened by means of catalytic agents. The addition of a little cobalt hydroxide (*q.v.*) to bleaching powder solution causes rapid evolution of oxygen. Finally, hypochlorites interact with acids by double decomposition (*cf.* p. 187) to give hypochlorous acid (see below). It is for the purpose of getting this acid, which is a powerful bleaching agent, that the hypochlorites are manufactured. The salts, such as bleaching powder, can be stored and transported easily, while the acid itself will not keep, except when largely diluted, and it consequently cannot be handled conveniently.

Preparation of Hypochlorous Acid: Hypochlorous Anhydride. — 1. The common method of obtaining the acid, HOCl, is by double decomposition, using a hypochlorite with some other acid (p. 187). When only a mixture of a chloride and a hypochlorite, such as is produced by the action of chlorine on a base (p. 189), is available, we have, simultaneously, the two reversible actions:

$$\begin{cases} KOCl + HNO_3 \leftrightarrows KNO_3 + HOCl, \\ KCl + HNO_3 \rightleftarrows KNO_3 + HCl. \end{cases}$$

But hypochlorous acid is a feeble acid, while hydrochloric acid is an active one, so that in the upper action the reversing tendency is very slight, while in the lower it is vigorous. Hence, by adding nitric acid, in amount barely sufficient for the liberation of the hypochlorous acid alone, and doing this in a very dilute solution, the object is attained. The potassium chloride is hardly affected. By gently warming the liquid a dilute solution of hypochlorous acid can be distilled off.

2. When chlorine is passed into water holding chalk in suspension, only the hydrochloric acid, produced by the interaction of the chlorine and water (equation 1, p. 189), acts upon the chalk. The

hypochlorous acid is too feeble to interact and can be obtained by subsequent distillation:

$$2Cl_2 + CaCO_3 + H_2O \rightarrow CaCl_2 + CO_2\uparrow + 2HOCl.$$

3. A third method is by addition of water to the anhydride.

The **anhydride of hypochlorous acid** (chlorine monoxide Cl_2O) may be obtained by passing chlorine gas over precipitated mercuric oxide. Each of the constituents of the oxide combines with chlorine:

$$HgO + 2Cl_2 \rightarrow HgCl_2 + Cl_2O.$$

The mercuric chloride then unites with another formula-weight of the mercuric oxide to form a basic mercuric chloride $HgO,HgCl_2$, which remains in the tube. The chlorine monoxide is a brownish-yellow gas. When slightly warmed it decomposes into its constituents with explosion. The gas dissolves in water very easily (200 : 1, by vol.). The yellow solution of hypochlorous acid which results:

$$Cl_2O + H_2O \leftrightarrows 2HOCl,$$

has a strong odor of chlorine monoxide. The combination is reversible, and, especially when the liquid is warm, a little of the gas escapes.

Properties of Hypochlorous Acid. — 1. Hypochlorous acid cannot be made, excepting in solution, or kept, excepting in dilute solution. This is in consequence of its tendency to decompose in three different ways, one of which, the liberation of the anhydride, has just been mentioned (see 3 and 4 below).

2. As an acid it neutralizes (p. 189) active bases, giving hypochlorites in a pure condition: $NaOH + HOCl \rightarrow NaOCl + H_2O$.

3. If the solution is concentrated, much of the hypochlorous acid changes gradually into chloric acid and hydrogen chloride. This occurs even in the dark: $3HOCl \rightarrow HClO_3 + 2HCl$.

4. When the solution is warmed, but more especially when it is exposed to sunlight, oxygen is evolved rapidly.

$$2HOCl \rightarrow 2HCl + O_2.$$

This decomposition always takes place in sunlight, whether the acid is present alone in the water, or along with other substances. Hence, the solution of chlorine in water (pp. 115, 189), which contains a small amount of hypochlorous acid, on being exposed to bright

sunlight, gives off bubbles of oxygen rapidly. This decomposition, since it removes one of the interacting substances in the reverse action, $Cl_2 + H_2O \leftrightarrows HCl + HOCl$, enables the interaction of chlorine and water to go on to completion. Consequently, the final liquid contains hydrochloric acid and water. Leaving out the intermediate steps again, the action *appears*, therefore, to be simply a decomposition of water by chlorine: $2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$.

5. In consequence of the ease with which it gives up oxygen, hypochlorous acid is a strong oxidizing agent (see below).

Hypochlorous Acid as an Oxidizing Agent: Bleaching.— Both **iodine** and **bromine** are oxidized by hypochlorous acid (either in pure solution or in the form of chlorine water, equation 1, p. 115), the former much more rapidly than the latter, $2HOCl + I_2 \rightarrow 2HOI + Cl_2$. Further oxidation to HIO_3 occurs immediately (see p. 198). Although iodine has less affinity for *hydrogen* than has chlorine (p. 172), this action shows that the relation towards *oxygen* is just the opposite. Here the iodine goes into combination and the chlorine is displaced.

It is on account of its oxidizing power that hypochlorous acid is used commercially in **bleaching**. It is not applied to paints, which are chiefly mineral substances, but to complex compounds of carbon, such as constitute the coloring matters of plants and of those artificial dyes whose manufacture has now become so gigantic an industry. It should be understood that the great majority of the complex compounds of carbon are colorless. Even a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material. **Indigo** ($C_{16}H_{10}N_2O_2$), which has a deep-blue color, is an example of a vegetable dye which is also made artificially. Hypochlorous acid oxidizes it to isatin, a yellow substance relatively pale in color:

$$C_{16}H_{10}N_2O_2 + 2HOCl \rightarrow 2C_8H_5NO_2 + 2HCl.$$

In ways just as definite as this, hypochlorous acid will change the composition of other colored substances, although, since we do not know the formulæ of all these substances, we cannot always write equations for the actions.

On account of the hypochlorous acid which is already present in chlorine water, this solution is a very efficient bleaching agent. The removal of this one of the factors in the reverse action (p. 183)

enables more of the acids to be produced from the chlorine and water until the whole of the halogen has been consumed.

As a rule, **bleaching** is actually carried out by liberating hypochlorous acid from bleaching powder by means of sulphuric acid:

$$Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix} + \begin{matrix}H \\ H\end{matrix}\!\!>(SO_4) \leftrightarrows CaSO_4 + \left.\begin{matrix}HOCl \\ HCl\end{matrix}\right\} \leftrightarrows H_2O + Cl_2.$$

Of course, temporarily, most of the hypochlorous acid interacts with the hydrochloric acid to give chlorine and water, but, as the residual hypochlorous acid loses its oxygen, the secondary action is again displaced backwards until the chlorine is all used up.

The yarn or cloth is first cleansed from fatty or oily material by boiling with soap solution. It is then immersed in bleaching powder solution, and finally in dilute sulphuric acid. Both solutions must be very weak in order that no interaction may occur with the fabric itself. The last two processes may be repeated, if the brownish or yellowish coloring material has not disappeared after the first treatment.

Hypochlorous acid can be used to bleach linen or cotton, because the body of these materials, apart from the small amount of coloring matter, is composed of compounds containing nothing but carbon, hydrogen, and oxygen. These compounds are very slowly affected by hypochlorous acid, unless too strong a solution is used, or the exposure to its influence is too long. That chemical action does occur is shown by the "rotting" of goods which have not been washed thoroughly after bleaching. Wool, silk, and feathers, on the other hand, are composed largely of compounds containing nitrogen in addition to the above three elements (see Dyeing). Their constituent material interacts as easily with hypochlorous acid as do the traces of coloring substances. Hence, since the fabric itself would be attacked by this agent, different means of bleaching have to be used for materials of this class.

It should be understood that a *cold dilute* solution of hypochlorous acid may be kept almost indefinitely and will not give up its oxygen spontaneously. The transfer takes place when, and only when, the acid comes in contact with some substance capable of uniting with oxygen.

Explanation of the Activity of Hypochlorous Acid as an Oxidizing Agent. — When hypochlorous acid decomposes into hydrochloric acid and oxygen, much heat is liberated (equation 1, below). The acid, therefore, possesses much more internal energy than do hydrogen chloride and free oxygen. On this account it brings to the task of oxidizing any substance more energy than does oxygen itself, and is therefore more efficient. Thus, free oxygen does not interact in the cold with indigo, or with bromine or iodine (see above), while hypochlorous acid oxidizes them rapidly. The heats of reaction show the difference very clearly. In equation (2), 1800 cal. is the amount of heat which would be liberated if indigo could be oxidized to isatin by oxygen gas. When hypochlorous acid is used, we obtain, in addition, the heat of decomposition of this substance (equation 1), so that the total heat liberated (equation 3), 20,400 cal., is ten times as great as in equation (2) where free oxygen is the oxidizing agent:

$$2HOCl = 2HCl\,(+\,2O) + 18{,}600 \text{ cal.} \qquad (1)$$

$$C_{16}H_{10}N_2O_2 + (2O) = 2C_8H_5NO_2 + 1800 \text{ cal.} \qquad (2)$$

$$C_{16}H_{10}N_2O_2 + 2HOCl = 2C_8H_5NO_2 + 2HCl + 20{,}400 \text{ cal.} \qquad (3)$$

By similar reasoning we explain the superiority of potassium permanganate over free oxygen for oxidizing hydrochloric acid (p. 111). Substances which are more active oxidizers than is free oxygen may be called active oxidizing agents.

Simultaneous, Independent Chemical Changes in the Same Substance. — As we have seen, hypochlorous acid undergoes three different changes. Some molecules decompose into water and chlorine monoxide (p. 191), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are independent of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the several simultaneous actions cannot be put in the same equation. The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence three separate equations are required in the present, and in all similar cases where all the proportions are not constant (see Perchlorates, p. 196). Successive actions,

like (1) followed by (2) in the next section (*cf.* p. 189), however, may be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (2) consumes what (1) produces.

Chlorates. — Like hypochlorous acid itself, the hypochlorites turn into chlorates. Thus, when chlorine is passed into a warm, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the potassium hypochlorite changes into **potassium chlorate** $KClO_3$ as fast as it forms. Since this action (equation 2) requires $3KClO$, the equation formerly given (p. 189) must be tripled:

$$3Cl_2 + 6KOH \rightarrow 3KCl + 3KClO + 3H_2O. \quad (1)$$
$$3KClO \rightarrow 2KCl + KClO_3 \quad (2)$$

Adding: $$3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O.$$

When the solution is cooled, the chlorate crystallizes out.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potassium chloride to the resulting solution, containing calcium chloride and **calcium chlorate** $Ca(ClO_3)_2$. The potassium chlorate, formed by double decomposition, crystallizes when the solution is cooled.

All chlorates are at least moderately soluble in water (see Table inside of front cover). Potassium chlorate is used in making fireworks, explosives, and matches. An intimate mixture with sugar ($C_{12}H_{22}O_{11}$) burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen of the sugar to form carbon dioxide and water. Detonating fuses for artillery are made of a mixture of this salt with antimony trisulphide (*q.v.*).

Chloric Acid $HClO_3$. — This acid may be obtained in solution in water, by adding the calculated amount of diluted sulphuric acid to a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \rightleftarrows BaSO_4 \downarrow + 2HClO_3.$$

The barium sulphate, being insoluble, is removed by filtration (*cf.* p. 188).

The solution may be concentrated (to about 40 per cent) by evapo-

ration, but must not be heated above 40°, as the acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, setting fire to paper (made of cellulose $(C_6H_{10}O_5)_n$) which has been dipped into it. It converts iodine into iodic acid, $2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$. When warmed beyond 40° the acid decomposes, giving **chlorine dioxide** and **perchloric acid**:

$$3HClO_3 \rightarrow H_2O + 2ClO_2 + HClO_4.$$

Chlorine Dioxide : Chlorous Acid.— **Chlorine dioxide** ClO_2 (see above) is a yellow gas which may be liquefied, and boils at + 10°. The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid (end of last section). Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as tests for chlorates, and distinguish them from perchlorates (*q.v.*). With water, chlorine dioxide gives a mixture of **chlorous acid** $HClO_2$ and chloric acid, and with bases a mixture of the **chlorite** and chlorate.

Perchlorates, Perchloric Acid, and Perchloric Anhydride. — When heated chlorates give **perchlorates**. Chlorates also give oxygen at the same time (p. 47):

$$\begin{cases} 2KClO_3 \rightarrow 2KCl + 3O_2, \\ 4KClO_3 \rightarrow 3KClO_4 + KCl. \end{cases}$$

These actions, like the three decompositions of hypochlorous acid (p. 191), are independent, and proceed simultaneously (p. 194). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a catalytic agent like manganese dioxide is added (p. 47). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at 15° less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 81) than the chlorates,

or hypochlorites: they are all soluble in water, and they are used in making matches and fireworks.

Pure **perchloric acid** $HClO_4$ explodes when heated above 92°. But, like other liquids, its boiling-point is lower when its vapor *is under reduced pressure* (*cf.* p. 79). At 56 mm. pressure it boils at 39°, a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by mixing potassium perchlorate and concentrated sulphuric acid and distilling the mixture cautiously in a vacuum:

$$KClO_4 + H_2SO_4 \rightleftarrows KHSO_4 + HClO_4\uparrow.$$

To secure the requisite low pressure, the ordinary distilling apparatus (Fig. 14, p. 26) is made completely air-tight, and is connected by a branch tube with a water-pump.

Perchloric acid is a colorless liquid, which decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable, however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. When liberated by concentrated sulphuric acid it does not at once give the yellow chlorine dioxide (p. 196).

Perchloric anhydride Cl_2O_7 may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture, $P_2O_5 + 2HClO_4 \rightarrow 2HPO_3 + Cl_2O_7$. Phosphoric anhydride is often used in this way for removing the elements of water from compounds. By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at 82° (760 mm.) and exploding when struck or too strongly heated.

Oxygen Acids of Bromine. — No oxides of bromine have been made, but the acids HBrO (hypobromous acid) and $HBrO_3$ (bromic acid) and their salts are familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, **potassium bromide** and **hypobromite** are formed:

$$Br_2 + 2KOH \rightarrow KBr + KBrO + H_2O.$$

When the solution is heated, the hypobromite turns into **potassium bromate** and bromide. The actions are exact parallels of the corresponding ones for chlorine (pp. 189, 195).

Aqueous **bromic acid** $HBrO_3$ may be made in the same way as

chloric acid (p. 195), or by the action of chlorine and water (equation 1, p. 115) on bromine:

$$5HClO + H_2O + Br_2 \rightarrow 2HBrO_3 + 5HCl.$$

The solution is colorless and has powerful oxidizing properties. Thus, it converts iodine into iodic acid: $2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2$. It appears, therefore, that iodine has more affinity for oxygen than has bromine.

The Oxide and Oxygen Acids of Iodine. — The following are the familiar acids and their corresponding salts:

HIO_3	Iodic acid,	KIO_3	Potassium iodate,
[HIO_4	Periodic acid],	$NaIO_4$	Sodium periodate,
H_5IO_6	Periodic acid,	$Na_2H_3IO_6$	Disodium periodate.

There is one oxide, iodic anhydride I_2O_5.

The **potassium** and **sodium iodates**, KIO_3 and $NaIO_3$, are found in Chili saltpeter. They may be made, in much the same fashion as are the chlorates and bromates (pp. 195, 197), by adding powdered iodine to a hot solution of potassium or sodium hydroxide.

Iodic Acid HIO_3 is formed by passing chlorine through iodine suspended in water. The action is parallel to that of chlorine on bromine water:

$$5HClO + H_2O + I_2 \rightarrow 2HIO_3 + 5HCl.$$

A still better way is to boil iodine with aqueous nitric acid (*q.v.*). The latter gives up oxygen readily, and is here used solely on this account. Hence it may be omitted from the equation, only the oxygen, of which it is the source, appearing:

$$I_2 + H_2O + 5O \rightarrow 2HIO_3.$$

In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, therefore, only the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At 170° it begins to give off water vapor ($2HIO_3 \rightleftarrows H_2O + I_2O_5$), leaving **iodic anhydride**. The latter is a white crystalline powder which may be raised to 300° before it, in turn, breaks up, giving iodine and oxygen.

Some **sodium periodate** ($NaIO_4$) is found in Chili saltpeter.

Chemical Relations. — The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen, in the order: F(19), Cl(35.5), Br(80), I (127). Each halogen will displace those following it from this kind of combination. In the case of the oxygen compounds, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable. The order of displacement in such compounds confirms this conclusion.

Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids.

The halogens when combined with metals and hydrogen are univalent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is higher. The maximum is shown in perchloric anhydride (Cl_2O_7), where chlorine appears to be heptavalent.

The formulæ of the acids might be written so as to retain the univalence:

$$H—Cl,\ H-O-Cl,\ H-O-O-Cl,\ H-O-O-O-Cl,\ H-O-O-O-O-Cl.$$

But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (see Hydrogen peroxide), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for $HClO_4$ is the most stable of the chlorine set. This reasoning, together with the heptavalence in Cl_2O_7, leads us to assume the valence seven in perchloric acid (see Periodic system). The structural formulæ (*cf.* p. 156) of some of these substances are therefore often written as follows:

$$H-Cl,\quad H-O-Cl,\quad H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cl}}=O,\quad Na-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{I}}=O.$$

Exercises. — 1. Assign to its proper class (pp. 124, 163, 189) each of the actions mentioned in this chapter.

2. Knowing that potassium fluosilicate (K_2SiF_6) is insoluble, how should you make chloric acid (p. 188)?

3. Make the equation for the interaction of chlorine with calcium

hydroxide in hot water (p. 195). How should you make zinc chlorate from zinc hydroxide ($Zn(OH)_2$)?

4. How should you make pure potassium hypochlorite from hypochlorous acid (p. 191)?

5. On what circumstances would the possibility of making barium chlorate by action of chlorine on barium hydroxide depend (p. 195)? Could pure barium chlorate be obtained easily by this means (see Table of solubilities)?

6. Make the equations for: (*a*) the preparation of potassium bromate; (*b*) pure aqueous bromic acid; (*c*) the interaction of iodine with aqueous potassium hydroxide in the cold, and when heated.

7. Make the equations for the interactions of chlorine dioxide with water, and with aqueous potassium hydroxide.

CHAPTER XVII

DISSOCIATION IN SOLUTION

THE employment of interacting substances in the form of solutions is so constant in chemistry, and the reasons for this are so cogent, that we must now resume the discussion of the subject of solution (*cf.* p. 96).

The present chapter will be devoted to giving the proofs that, to speak in terms of the molecular hypothesis, the molecules of **acids, bases, and salts** in aqueous solutions, are **actually dissociated into parts** by the solvent. This will be shown by consideration, successively, of certain peculiarities in the **chemical behavior**, and the **freezing-points** of the solutions of these substances. We shall see that **these parts coincide in composition with the radicals.**

Some Characteristic Properties of Acids, Bases, and Salts, Shown in Aqueous Solution. — **Acids all** contain hydrogen (p. 64). In aqueous solution, if soluble, they are sour in taste, they turn blue litmus red, and their hydrogen is displaced by certain metals (p. 65), and has the properties of a radical. By the last statement is meant that it very readily exchanges places with other radicals in reversible double decompositions (p. 187). Many other bodies, like sugar, kerosene, and alcohol, contain hydrogen also, but not one of them shows all of these properties. Again, **all salts** are made up of two radicals, and the reversible double decompositions into which they enter with acids, bases, and other salts, consist in exchanges of these radicals. Other substances may include the same combinations of atoms, but in their actions these groupings are often disregarded. Thus, sodium chloride and silver nitrate exchange radicals completely (p. 187), and, in dilute solution, hydrogen chloride and sodium hydrogen sulphate do so partially (p. 118). But sodium chloride and nitroglycerine $C_3H_5(NO_3)_3$ do not interact at all. The latter is not a salt, although it contains the same proportion of nitrogen to oxygen as does any nitrate.

Furthermore, it is chiefly **in aqueous solution** that these special prop-

erties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, we mix together ammonium carbonate and partially dehydrated cupric nitrate, and apply heat, a violent interaction begins. An immense cloud of smoke and gas is thrown out of the tube, and the substance remaining is either black, or reddish, in parts, according to the proportions of the substances employed. The residue contains cupric oxide, and sometimes red cuprous oxide (Cu_2O). The gas is tinged red by the presence of nitrogen tetroxide (NO_2), while a more careful examination would show that it contained carbon dioxide, nitrogen, nitrous oxide (N_2O), water vapor, and perhaps still other products. The *contrast, when the substances are dissolved in water* before being brought in contact with one another, is very great. A pale-green precipitate is formed at once, and rapidly settles out. On examination, this turns out to be a carbonate of copper (basic), while evaporation of the solution furnishes us with ammonium nitrate. There are only two main products, and the essential part of the action in solution may be represented by the equation:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3 + 2NH_4NO_3.$$

In the interaction between the dry substances the molecules are completely disintegrated, and the whole change is very complex. In the action in water no heating is required, the substances are neatly broken apart, certain groups of atoms, which we call radicals, are transferred as wholes from one state of combination to another, and the rearrangement takes place in a machine-like manner. Contrasts like this between the interactions of anhydrous and dissolved bodies are very common.

Many compounds, however, do not show any change in behavior when dissolved in water. Sugar, for example, is, as a rule, more readily acted upon in the absence of any solvent. Then again, while water is not the only solvent which has the effect we have just described, the majority of solvents, if they affect chemical change at all, simply retard it. Thus the union of iodine and phosphorus in the absence of a solvent takes place spontaneously with a violent evolution of heat. When the elements are dissolved in carbon bisulphide, before being mixed, the action is much milder, although the product is the same (phosphorus tri-iodide). The diminution in the concentration of the ingredients has decreased the speed of the action

in the normal way (p. 180). That water and some other solvents have a specific influence tending to increase the apparent activity of certain classes of substances, shows that a special explanation of the phenomenon must be found.

Summing up these points we see that the peculiarity of acids, bases, and salts *in aqueous solution* is that each compound always splits in the same way. Thus, cupric nitrate always gives changes involving Cu and NO_3 and never interacts so as to use CuN_2 and O_3, or CuO_2 and NO_2, as the basis of exchange. Similarly, dilute acids always offer hydrogen in exchange, and so nitric acid behaves as if composed of H and NO_3, and sulphuric acid as if composed of 2H and SO_4, and never as if made up of HSO and HO_3, or H_2S and O_4. The sour taste and the effect upon litmus seem to be properties of this easily separable hydrogen, for they are shown only by acids. The result is that we can make a list of the units of exchange, such as H, OH, NO_3, CO_3, SO_4, Cu, K, and Cl, employed by acids, bases, and salts in their interactions. The molecule of each compound of these classes contains at least two of them. Even when these units contain more than one atom, their coherence is as noticeable within this class of actions, as is the permanence of the atomic masses themselves in all actions.

The question raised in our minds is whether solution in water alters the character of the molecule, simply by producing a sort of *plane of cleavage* in it which creates a predisposition to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts consisting of the above units of exchange, and leaves subsequent chemical actions to occur by cross-combination of these fragments. The fact that the dissolved substances can be recovered by evaporation of the liquid does not demonstrate that they have not been decomposed temporarily while in solution. The alteration which the water produces, whatever it be, will naturally be reversed when the water is removed. Since our question involves nothing but the counting of particles, the number of which would be much greater in the event that actual subdivision of molecules is the explanation, it can be answered by a study of the physical properties of solutions. Several physical properties can be used, and they give concordant answers to the question. We shall confine ourselves here, however, to the evidence furnished by the freezing-points of solutions.

Freezing-Points of Solutions.—Every pure liquid has a definite temperature at which it freezes. Thus, pure water freezes at 0° and benzene at 6°. The presence of a foreign, dissolved body, however, lowers the freezing-point. Thus, sea-water is harder to freeze than fresh water. The freezing-points of solutions of the same substance are found to be depressed below that of the solvent in proportion to the concentration of the solute.* Thus, in one set of experiments, solutions of sugar containing 11.4 g., 22.8 g., and 34.2 g. of sugar to 100 g. of water were found to freeze at − 0.62°, − 1.23°, and − 1.85°, respectively.

In everyday life we scatter salt on ice to melt it. The salt dissolves in the moisture on the surface, and the ice cannot exist in presence of this solution at 0° (p. 78). It melts, absorbing heat in doing so, until the temperature of the mixture reaches that of a freezing, saturated solution of salt (about − 21° = − 6° F.). When the existing temperature is lower than this, the salt has no effect on the ice. **Freezing mixtures**, being usually mixtures of ice with various soluble substances, work in accordance with this principle.

Laws of Freezing-Point Depression.—The depression in the freezing-point is directly proportional to the weight of dissolved substance in a given amount of the solvent. The depression is inversely proportional to the amount of solvent. Thus, if we double the concentration of the solution, the depression in the freezing-point is doubled. Further, **equal numbers of molecules of different solutes in the same quantity of solvent give equal depressions.** Or, in other words, the depression is proportional to the concentration of the molecules of the solute. Thus, solutions containing 342 g. of sugar ($C_{12}H_{22}O_{11}$†), or 46 g. of alcohol (C_2H_6O), or 74 g. of methyl acetate $CH_3(C_2H_3O_2)$, in 1000 g. of water, being weights which contain equal numbers of molecules, show a depression below the freezing-point of water of about 1.89° in each case. That is, such solutions all freeze close to − 1.89°. This depression, produced by a mole of the solute in 1 l. of water, is called the **molecular depression constant**, and has a different value for each solvent. For solutions of the same

* The ice which separates during the freezing consists, as a rule, of the pure solvent, and the solute does not enter into it. Only when this is the case does this law represent the facts.

† $12 \times 12 + 22 \times 1 + 11 \times 16 = 342$.

molecular concentration in benzene the depression is 4.9°, in phenol (carbolic acid) 7.5°. Combining these facts in one expression:

$$\left.\begin{array}{r}\text{The observed depression}\\ \text{in an } \textit{aqueous} \text{ solution}\end{array}\right\} = 1.89^\circ \times \frac{\text{Wt. of Solute}}{\text{Mol. Wt. of Solute}} \times \frac{1000}{\text{Wt. of Solvent.}}$$

For other solvents, the corresponding value of the depression constant must be substituted for 1.89°.

These laws describe the facts most exactly when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent. Even so, however, *acids, bases, and salts dissolved in water present many apparent exceptions* and must be discussed separately (see below).

It will be noted that, when the other factors in the foregoing equation are known or observed, **the molecular weight of the solute may be determined.** The fact makes possible the determination of this constant for substances which are not volatile (see Hydrogen peroxide).

Freezing-Points and Dissociation in Solution. — The substances which present the most conspicuous **exceptions** to the above rules are acids, bases, and salts in aqueous solution. With most of these, the depression produced is greater than we should expect from the concentration of the solution. Thus, in an actual experiment, two equi-molar solutions were compared. One contained one mole (74 g.) of methyl acetate, and the other one mole (58.5 g.) of sodium chloride, each dissolved in 2000 g. (2 liters) of water. The freezing-points observed were:

Pure water	0.000°	Pure water	0.000°
Sol. of methyl acetate .	−0.970°	Solution of salt . . .	−1.678°
Depression	0.970°	Depression	1.678°
			0.970°
		Excess depression by salt	0.708°

The solution of methyl acetate, as it contained only 0.5 moles of the solute per liter of water, showed, as it should do, about half the average molecular depression (1.89°, p. 204). This is typical of the class of substances showing normal behavior. Sugar, alcohol, and hundreds of other substances, in solutions of the same molar concentration, would have given the same value.

The freezing-point of the salt solution, however, was much lower.

If this solution had really contained the same concentration of dissolved molecules as the other solution, its depression would have been 0.970° likewise. The number of molecules in the solution must therefore have been greater than we should have expected from the number of molecules taken. In other words, a portion of the molecules of the salt must have been broken up, and the excess depression, 0.708°, must have been due to the extra molecules produced by dissociation. Now sodium chloride molecules cannot give more than two particles each, and the depression is proportional to the number of particles. It follows, therefore, that $\frac{708}{970}$, or 0.732 (73.2 per cent) of the molecules were dissociated.

This result is typical also. Acids, bases, and salts, of which one mole is dissolved in two liters of water, are found to give irregular values, all more or less in excess of 0.970°. Those which contain but two radicals, like sodium chloride (NaCl) and potassium nitrate (KNO_3), give values between 0.970° and $2 \times 0.970°$. Substances like calcium chloride ($CaCl_2$) and sodium sulphate (Na_2SO_4) give depressions approaching three times the normal value: their molecules contain three radicals. The excess depression depends, therefore, upon the number of particles which each molecule can furnish, and upon the proportion of all the molecules which is dissociated into these fragments.

In the case of an acid, base, or salt, the depression is not strictly proportional to the concentration. Thus, one mole of salt in *four* liters of water does not give half the depression of the two-liter solution (0.839°) but *somewhat more* (about 0.844°). The same method of calculation indicates, therefore, a greater degree of dissociation (about 79 per cent) in the more dilute solution (see Ionic equilibrium).

Acids, bases, and salts, so far as they are soluble in materials like toluene, benzene, chloroform, and carbon bisulphide, exhibit simply normal depressions in these solvents. It appears, therefore, that, in many solvents, dissociation does not take place. In common experience it is encountered only in solutions in water, and, perhaps, alcohol.

The freezing-point is only one of *four* properties of solutions which can be used for determining the numbers of molecules present. Numerous measurements show that aqueous solutions of acids, bases, and salts not only have abnormal freezing-points, but also abnormal

osmotic pressures (*cf.* p. 101) and abnormal boiling-points. The electrical conductivity is the fourth property which gives the required information (see Chap. xix). Now, when we observe the behavior of the same solution in each of these four ways, and calculate the degree of dissociation from the result of each measurement, we find that the values obtained are usually identical, within the limits of error to which the methods are liable. Thus the indications of dissociation found in the chemical behavior of acids, bases, and salts (p. 203) are fully confirmed by a study of the physical properties of their solutions.*

Applications: The Constitution of Solutions of Acids, Bases, and Salts. — The composition of solutions which are normal or abnormal, in respect to osmotic pressure, freezing-point, and boiling-point, may be shown thus:

Solutes.	Dissolved in Water, Alcohol, etc.	Dissolved in Toluene, Chloroform, etc.
Acids, bases, salts	Abnormal	Normal
Other substances	Normal	Normal

It appears that water and some other solvents have the power of decomposing acids, bases, and salts. Such solvents have, in fact, an effect on these materials that resembles, outwardly at least, the effect which heat has on many substances (*e.g.* p. 81), **they cause dissociation:**

$$NaCl \rightleftarrows (Na) + (Cl).$$

In consequence of this, our view of the nature of an aqueous solution of hydrogen chloride (HCl), or common salt (NaCl), or sodium hydroxide (NaOH), or any of the substances of the classes which these represent, may now be stated in definite terms. Such a solution contains, besides undivided molecules of the solute, at least two other kinds of material, H, Na,† Cl, OH, etc., which result from the

* Recent observations, showing that in some cases rapid double decompositions of the normal kind take place in solutions which exhibit no physical evidence of the existence of dissociation, demonstrate that it would have been unsafe to infer dissociation from chemical evidence alone.

† The objection that separate atoms of sodium could not remain free in water, will be disposed of later.

breaking up of the molecules. We shall see that these subdivisions of the original molecules have distinct physical and chemical properties of their own. The descriptions of the "properties" of the solutions, as they used to be given in chemistry, were really a confused statement of the properties of the different components of a mixture.

The *free* radicals, of whose existence we have thus become convinced, constitute a new set of materials (with appropriate names. See p. 224). Thus the hydrogen radical of acids, although a form of uncombined hydrogen, differs totally from the gas which is composed of the same material. The gas has no sour taste or effect upon litmus: these are properties of the free radical. The gas is very slightly soluble in water, while the hydrogen radical exists as a separate substance only in solution. Again, substances with the composition of the radicals NO_3 and SO_4 are not known at all except in solutions.

Exercises. — 1. What depression in the f.-p. of water will be produced by dissolving 10 g. of bromine in 1 kg. of this solvent?

2. What depressions in the f.-p. of benzene and of phenol would be produced by 10 g. of bromine to 1 kg. of the solvent, if no chemical action took place?

3. What is the molecular depression-constant of a solvent in which 5 g. of iodine in 500 g. of the solvent lowers the f.-p. 0.7°?

4. What is the degree of dissociation of zinc sulphate, if 5 g. of it dissolved in 125 g. of water produce a lowering of 0.603° in the f.-p.?

CHAPTER XVIII

OZONE AND HYDROGEN PEROXIDE

A FRESH, penetrating odor, resembling that of very dilute chlorine, was noticed by van Marum (1785) as being perceptible near an electrical machine in operation. Schönbein (1840) showed that the odor was that of a distinct substance, which he named ozone (Gk. ὄζειν, to smell), and he discovered a number of ways of obtaining it. It is very questionable whether there is any ozone in the air, excepting temporarily in the immediate neighborhood of a natural or artificial discharge of electricity.

Preparation of Ozone O_3. — The most satisfactory way of preparing ozone is to allow electric waves to pass through oxygen. The apparatus (Fig. 50) consists of two co-axial glass tubes, between

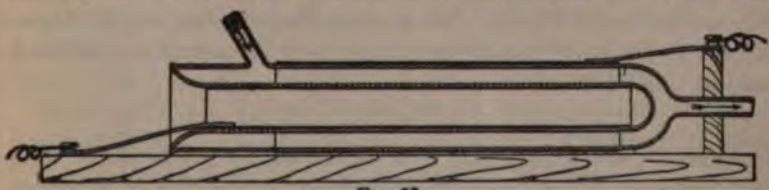


FIG. 50.

which the oxygen flows. The waves are generated by connecting an outer layer of tinfoil on the outer tube, and an inner layer of tinfoil in the inner tube with the poles of an induction coil. With dry, cold oxygen, about 7.5 per cent of the gas is turned into ozone.

Ozone is found in the oxygen generated by electrolysis of dilute sulphuric acid (see p. 216). It arises during the slow oxidation of phosphorus by the air, resulting, probably, from the decomposition of unstable, highly oxidized bodies which are formed during the action. Ozone is formed also when a jet of burning hydrogen, or an electrically heated loop of platinum wire is immersed in liquid oxygen. Oxygen containing as much as 15 per cent of it is produced by the interaction of fluorine and water (p. 170).

Physical Properties of Ozone. — Ozone is a gas of blue color. It boils at − 119°, so that when a mixture of oxygen and ozone is led through a U-tube immersed in liquid oxygen (− 182.5°), the ozone collects in the tube as an opaque, deep-blue fluid. Ozone is much more soluble in water than is oxygen. At 12°, 100 volumes of water would dissolve 50 volumes of the gas at one atmosphere pressure.

Chemical Properties of Ozone. — The density of ozone is one-half greater than that of oxygen. Its molecular weight is therefore 48, and its formula O_3. Ozone is relatively stable when mixed with much oxygen. When the ozonized oxygen is heated, however, the ozone is decomposed at about 250–300°. The action for its formation:

$$3O_2 \rightleftarrows 2O_3$$

is therefore reversible. As the equation shows, three volumes of oxygen give two of ozone. There is also an absorption of much energy from the electric waves, or, in other methods of making it, from the concomitant chemical changes: $O + O_2 = O_3 - 32{,}400$ cal.

Ozone is a much more active oxidizing agent than oxygen. Mercury and silver, which are not affected by the latter, are converted into oxides by the former. Silver gives the peroxide, Ag_2O_2. Paper dipped in starch emulsion containing a little potassium iodide is used as a test for ozone:

$$O_3 + 2KI + H_2O \rightarrow O_2 + 2KOH + I_2.$$

The iodine gives a deep-blue color to the starch (*cf.* p. 165). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances. Ozone also removes the color from organic dyes, such as indigo, by oxidizing them (*cf.* p. 192). Its activity as an oxidizing agent, like the similar activity of hypochlorous acid, is due to the fact that it contains much more energy than oxygen.

Ozone is used commercially in bleaching oils and in purifying starch. It is employed also for sterilizing drinking water in Lille and other cities.

Hydrogen Peroxide H_2O_2.

Hydrogen peroxide is found in minute amounts in rain and snow. It is formed in small quantities, in a way not at present fully understood, when moist metals rust.

Preparation of Hydrogen Peroxide.—When sodium peroxide (*q.v.*) is added, a little at a time, to a dilute acid, hydrogen peroxide is set free and remains dissolved in the liquid.

$$Na_2O_2 + 2HCl \leftrightarrows 2NaCl + H_2O_2.$$

When hydrated barium peroxide ($BaO_2,8H_2O$) is shaken with cold, dilute sulphuric acid a similar action takes place:

$$BaO_2 + H_2SO_4 \leftrightarrows BaSO_4\downarrow + H_2O_2.$$

Phosphoric acid is largely employed instead of sulphuric acid in the commercial manufacture of hydrogen peroxide, and great care is taken to precipitate the other products and all impurities from the solution.

An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O \leftrightarrows BaCO_3\downarrow + H_2O_2.$$

Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure (p. 197). It is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 68 mm. pressure, the water begins to pass off first (at about 45°). The last portion of the liquid boils at 84–85° and is almost all hydrogen peroxide.

By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

Physical Properties. — Hydrogen peroxide is a syrupy liquid of sp. gr. 1.5. It blisters the skin, and, when diluted, has a disagreeable metallic taste. It has been frozen (m.-p. − 2°).

Chemical Properties. — Hydrogen peroxide (100 per cent) is very unstable, and decomposes slowly even at − 20°. The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid increases its stability. Free alkalies and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Addition of powdered metals, of manganese dioxide, or of charcoal causes effervescence even in dilute solutions, and oxygen escapes:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Since the substance cannot be vaporized, even at low pressure, without some decomposition, its molar weight has been determined by the freezing-point method. The freezing-point of a 3.3 per cent solution in water was $-2.03°$. Substitution of these data in the formula (p. 205) gives 31.8 g. as the molar weight. Now the formula HO corresponds to a molar weight of 17 and H_2O_2 to one of 34. It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a feeble acid. As an acid it enters into double decomposition readily, and the peroxides are really salts in which the negative radical is O_2''. Thus, when hydrogen peroxide is added to solutions of barium and strontium hydroxides, the hydrated peroxides appear as crystalline precipitates:

$$Sr(OH)_2 + H_2O_2 \rightleftarrows 2H_2O + SrO_2.$$

The precipitation involves another equilibrium: $SrO_2 + 8H_2O \rightleftarrows SrO_2, 8H_2O$ (solid).

The formation of a beautiful blue substance by the action of hydrogen peroxide upon dichromic acid is used as a test. The test is carried out by adding a drop of potassium dichromate to an acidulated solution of the peroxide. The acid interacts with the dichromate, giving free dichromic acid:

$$H_2SO_4 + K_2Cr_2O_7 \rightleftarrows H_2Cr_2O_7 + K_2SO_4.$$

The composition of the blue substance, which is very unstable and quickly decomposes, is not certainly known, so that no equation for its formation can be given. The blue substance has the property, unusual in inorganic compounds, of dissolving much more readily in ether than in water. It is also much less unstable when removed from the foreign materials in the aqueous solution. Hence the test is rendered more delicate by extracting the solution with a small amount of ether. In the ethereal layer the color of the compound is more permanent, as well as more distinctly visible on account of the greater concentration.

Hydrogen peroxide is a much more active oxidizing agent than is free oxygen. This would be expected from the fact, that it contains so much more internal energy than the water and oxygen into which it decomposes (p. 194), that 23,100 cal. are liberated in the decomposition of one mole. Thus, it liberates iodine from hydrogen iodide, an action which, in presence of starch emulsion (*cf.* p. 165), is used as a test for its presence:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2.$$

It converts sulphides into sulphates. The white lead (*q.v.*) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide, $Pb_3(OH)_2(CO_3)_2 + 3H_2S \rightarrow 3PbS + 4H_2O + 2CO_2$. This may be oxidized to white lead sulphate by means of hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O,$$

and in this way the original tints of the picture may be practically restored. Organic coloring matters are changed into colorless substances by an action similar to that of hypochlorous acid (*cf.* p. 192). Hence hydrogen peroxide is used for bleaching silk, feathers, hair, and ivory, which would be destroyed by this more violent agent. The products of its decomposition, being water and oxygen only, are harmless, and, on this account, it is used as a bactericide in surgery.

Hydrogen peroxide exercises the functions of a reducing agent in special cases, also. Thus, silver oxide is reduced by it to silver:

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2.$$

A solution of potassium permanganate, in which the permanganic acid has been set free by an acid: $KMnO_4 + H_2SO_4 \rightleftarrows HMnO_4 + KHSO_4$, is rapidly reduced. The permanganic acid, with excess of sulphuric acid, tends to undergo the first of the following changes, *provided a substance*, such as hydrogen peroxide, *is present which can take possession of the oxygen that would remain as a balance*:

$$2HMnO_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + 3H_2O\ (+\ 5O) \qquad (1)$$
$$(5O) + 5H_2O_2 \rightarrow 5H_2O + 5O_2 \qquad (2)$$
$$2HMnO_4 + 2H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + 8H_2O + 5O_2$$

Exercises. — 1. What volume of ozone will be taken up by 100 c.c. of water at 12° from a stream of oxygen containing 7.5 per cent of ozone (p. 103)?

2. At what temperature will a ten per cent solution of hydrogen peroxide freeze (p. 205)?

3. Write the thermochemical equations for oxidation of indigo by ozone (pp. 194, 212), and by hydrogen peroxide.

CHAPTER XIX

IONIZATION

Introductory. — As we have seen, acids, bases, and salts, when dissolved in water, interact with one another by *interchanging radicals* (p. 201). We have also learned that the same solutions have abnormal values for their freezing-points and for two other properties. These facts indicate *dissociation into the radicals* (p. 207). Now precisely these solutions have a property which is not shared by any other solutions, namely, that of being *conductors of electricity and suffering chemical decomposition by the passage of the current.* Such solutions are called, in consequence, **electrolytes**, and the process is named **electrolysis** (ἤλεκτρον, and λύειν, to loosen, *i.e.* to decompose, by means of electricity). Now the natural inference from the foregoing facts is that **the electricity is carried by the liberated radicals.** Our first aim in the present chapter is to show **by a study of the chemical changes taking place in electrolysis** that this inference is correct. We then proceed to discuss the **hypothesis of ions**, by means of which these facts are harmonized with the molecular hypothesis. Next, we apply the hypothesis to **the explanation of electrolysis**, to the **equilibrium between the ions and the remaining, undissociated molecules**, and to **conductivity phenomena** as a means of measuring the **fraction ionized.** Finally we deduce the relation between extent of ionization and **chemical activity.**

Incidentally, the facts to be given provide the means of understanding the electrolytic processes, many of them of great importance in chemical industries, to which frequent reference is made in later chapters.

Non-Electrolytes.—To clear the ground, we should first note the fact that only solutions (as a rule) possess both of the properties in question, namely that of conducting and that of being decomposed by the current. Some substances, notably the metals and materials like carbon, are conductors. But they are not changed

chemically by the current. Again, single substances, even when they are such as, if mixed, yield electrolytes, are not conductors at ordinary temperatures. Thus hydrogen chloride, whether gaseous or liquefied, is a nonconductor, and water is a very feeble conductor, although the solution of the two conducts exceedingly well. Dry acids, bases, and salts, except when at a high temperature and fused, are likewise nonconductors. Furthermore, even amongst solutions, not all are conductors. Solutions of sugar and other substances of the same class (p. 205), which have normal freezing-points, are nonconductors. Only solutions of acids, bases, and salts in certain specified solvents, of which the commonest is water, are electrolytes at ordinary temperatures.

Chemical Changes Taking Place in Electrolysis: at the Electrodes. — When the wires from a battery are attached to platinum plates immersed in any electrolyte (*e.g.* Fig. 21, p. 64), we observe that the products appearing at the two electrodes are always different. They may be of several kinds physically, and will be secured for examination variously according to their nature. Thus, when they are **gases** which are not too soluble, they may be collected in inverted tubes filled with the solution. **Solids**, if insoluble in the liquid, will either remain attached to the electrode or fall to the bottom of the vessel as precipitates. **Soluble substances** on the other hand will usually not be visible. They may be handled by interposing a porous partition of some description which will restrain the diffusion of the dissolved body away from the neighborhood of the electrode, while not interfering appreciably with the passage of the current. Surrounding one electrode with a porous battery jar is a convenient method for effecting this.

Of the various illustrations which we have encountered, the electrolysis of hydrochloric acid (p. 64) happens to have been the only one which delivered both components of the solute with a minimum of modification at the electrodes:

$$\text{Neg. wire, } H_2 \longleftarrow H.Cl \longrightarrow Cl_2\text{, Pos. wire.}$$

Hydrogen does not interact with water, and chlorine interacts very slightly, so that the molecular substances H_2 and Cl_2 are promptly formed from the elements H and Cl which are liberated. The chlorides, bromides, and iodides of those metals which do not interact with water give equally simple results:

$$\text{Neg. wire, } Cu \longleftarrow Cu.Br_2 \longrightarrow Br_2\text{, Pos. wire.}$$

Thus, in electrolysis, the solute seems to *split into its radicals*, and the radical, if it does not interact with water, is set free. A substance thus set free is called a **primary product** of the electrolysis. In the foregoing instances both products are primary.

Usually the chemical change is more complex. Thus, when dilute sulphuric acid is electrolyzed, hydrogen and oxygen are liberated at the negative and positive electrodes, respectively. But these products do not account for the whole of the constituents (H_2SO_4). We therefore proceed to examine the materials in solution round the electrodes. It is found that, as the action progresses, sulphuric acid accumulates round the positive wire, while the liquid in the neighborhood of the other pole is gradually depleted of this substance. In view of this fact we easily explain the phenomenon. Evidently the substance divides into its radicals, H and SO_4, but SO_4, not being a known substance, must interact with the water to produce sulphuric acid and oxygen: $2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2$. The whole change may therefore be tabulated as follows:

$$\text{Neg. Wire, } H_2 \longleftarrow H_2.SO_4 \longrightarrow O_2 \text{ and } H_2SO_4\text{, Pos. Wire.}$$

Hence the hydrogen is a primary product, but the oxygen and sulphuric acid are **secondary products**. All acids give hydrogen alone at the negative electrode, whatever may be the product at the positive.

If we electrolyze cupric nitrate solution, we obtain a red deposit of metallic copper on the negative plate and at the positive end oxygen and nitric acid are formed. We infer, therefore, that the division of the original molecule was into Cu and NO_3, but that the latter interacted with the water: $4NO_3 + 2H_2O \longrightarrow 4HNO_3 + O_2$:

$$\text{Neg. Wire, Cu.} \longleftarrow Cu.(NO_3)_2 \longrightarrow O_2 \text{ and } HNO_3\text{, Pos. Wire.}$$

With a solution of potassium nitrate we find hydrogen and oxygen appearing at the negative and positive electrodes respectively. Litmus paper, however, shows the presence in the solution of a base (potassium hydroxide, KOH) at the negative and an acid (nitric acid) at the positive end. Secondary chemical changes have occurred at both poles. We infer that the parts of the parent molecules are K and NO_3. The former, since it resembles sodium (p. 66), instead of being liberated, gave rise to free hydrogen and potassium hydroxide :

$$\text{Neg. Wire, } H_2 \text{ and KOH} \longleftarrow K.NO_3 \longrightarrow O_2 \text{ and } HNO_3\text{, Pos. Wire.}$$

We are confirmed in these conclusions when we employ a pool of mercury in place of the negative wire. A portion of the potassium is then found to have dissolved in the mercury and escaped interaction with the water.

Having now before us the results of electrolyzing some typical substances, we bring these results into relation with the facts described in the last chapter. Acids contain hydrogen which possesses certain specific properties (p. 201), and by electrolysis they all divide so as to give up *this constituent alone* at one electrode. The evidence that the other radical has different electrical properties which carry it to the opposite plate is conclusive. Again, salts undergo double decomposition in which they exchange radicals with acids, bases, and other salts (p. 201), and we find that it is **these very radicals which are withdrawn from the solution by the influence of the electricity.** Furthermore, the radicals exist free in the solution, being formed by dissociation of the molecules (p. 207). Hence **the function of the electricity seems simply to consist in sifting apart the two kinds of free radicals** which each solution contains. It only remains for us to construct an hypothesis (see below) to account for the sifting action of the current. Before turning to this explanation of the phenomena, however, there is one question which may be answered in passing. Since a solution may eventually be cleared of all the hydrochloric acid, for example, which it contains, we should like to know how the free radicals in the center of the cell reach the electrodes.

Ionic Migration.— To know how the free radicals reach the electrodes, all that is necessary is to take a material, one (or both) of whose radicals is a colored substance, and watch the movement of the colored material as it drifts towards the electrode. Most salts which give colored solutions are suitable. In very dilute cupric sulphate solution, for example, a freezing-point determination shows that the depression has practically double the normal value. In other words, the dissociation into the radicals, $CuSO_4 \rightleftarrows (Cu) + (SO_4)$, is almost complete. Now, the blue color of the solution cannot be due to the few remaining molecules of $CuSO_4$, for anhydrous cupric sulphate is colorless. Nor is it due to the color of the (SO_4) radicals, for dilute potassium sulphate and dilute sulphuric acid are both colorless. On the other hand, all cupric salts, in dilute solution, have the same tint. The color is therefore that of the free cupric

radical (Cu). In order most clearly to see the motion of the cupric radical, we place the cupric sulphate solution in the middle of the space beween the electrodes, and place between it and the latter a colorless conducting solution. The motion of the blue material across the boundary may then be easily observed.

The most convenient arrangement is to dissolve the cupric sulphate in warm water containing about 5 per cent of agar-agar, and to fill with this mixture the lower part of a U-tube (Fig. 51). The setting of the jelly prevents subsequent mixing of the cupric sulphate system of materials with the rest of the filling of the tube, and the consequent disappearance of the boundary. A few grains of charcoal may be scattered on the surface of the jelly to mark the present limits of the colored substance, and a solution of some colorless electrolyte, such as potassium nitrate, is added on each side. To prevent agitation of the liquid by the effervescence at the electrodes, it is well to use agar-agar with the lower part of the colorless liquid also. The whole is finally placed in ice and water, to prevent melting of the jelly by the heat caused by resistance, and the current is then turned on.

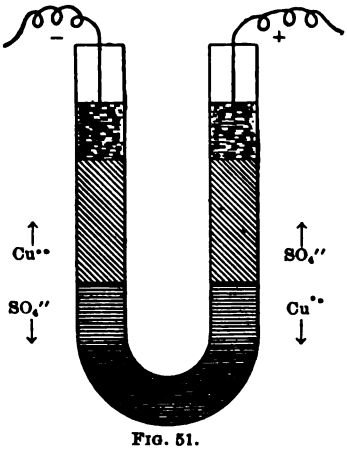


FIG. 51.

After a time, we observe that the blue cupric radicals ascend above the mark on the negative and descend away from it on the positive side. In each case there is no shading off in the tint. The motion of the whole aggregate of colored radicals occurs in such a way that, if the contents of the tube were not held in place by the jelly, we should believe that a gradual motion of the entire blue solution was being observed. With a current of 110 volts, and a 16-candle power lamp in series with the cell, the effect becomes apparent in a few minutes.

Although the (SO_4) radicals are invisible, we may safely infer that they are drifting towards the positive electrode. Indeed, this can be demonstrated by interposing a shallow layer of jelly containing

some barium salt a little distance above the charcoal layer on the positive side. When the (SO_4) reaches this, barium sulphate begins to be precipitated and the layer becomes cloudy. In similar ways the progress of other colorless ions may be rendered visible.

It appears, therefore, that electrolysis is not a local phenomenon, going on round the electrodes only, but that the **whole of the products of the dissociation of the solute are set in motion.** It is on account of this remarkable property of traveling or **migrating** towards one or other of the electrodes that the individual atoms (like Cu), or groups of atoms (like SO_4), have been named **ions** (Gk. ἰών, going). The term was first applied by Faraday to the materials liberated round the electrodes.

Different ionic substances move with different speeds when propelled by the same current. The hydrogen radical of acids (H) is the most speedy, the hydroxyl radical of bases (OH) comes next. The actual speeds of several ions, in dilute solutions at 18°, when driven by a potential difference of 1 volt between plates 1 cm. apart, expressed in cm. per hour is: H 10.8, OH 5.6, Cu 1.6, SO_4 1.6, K 2.05, Cl 2.12.

The Hypothesis of Ions. — That the molecules of certain classes of substances, although seemingly without chemical interaction with the water in which they are dissolved, should nevertheless be decomposed by the influence of the water, is strange, but not inconceivable. Heating produces a somewhat similar effect on many substances. The novel fact, for which an explanation is demanded, is that the molecules of the products of the dissociation appear to be attracted by electrically charged plates, which have been lowered into the solution, while molecules of dissolved sugar, for example, are not so attracted. Now the only bodies which we find to be conspicuously attracted by electrically charged objects are bodies which are *already provided with electric charges of their own.* Thus we are led to add to the molecular hypothesis the assumption that substances which undergo dissociation in solution **divide themselves into a special kind of electrically charged molecules.**

Since the solution, as a whole, has itself no charge, equal quantities of positive and negative electricity must be produced:

$$HCl \rightleftarrows \overset{+}{H} + \overset{-}{Cl} \quad NaCl \rightleftarrows \overset{+}{Na} + \overset{-}{Cl} \quad NaOH \rightleftarrows \overset{+}{Na} + \overset{-}{OH}.$$

This means that bivalent radicals, on dissociation, will become ions carrying a double charge and trivalent ions must carry a triple charge:

$$CuCl_2 \rightleftarrows \overset{++}{Cu} + 2\overset{-}{Cl} \qquad CuSO_4 \rightleftarrows \overset{++}{Cu} + \overset{--}{SO_4}$$

$$K_2SO_4 \rightleftarrows 2\overset{+}{K} + \overset{--}{SO_4} \qquad FeCl_3 \rightleftarrows \overset{+++}{Fe} + 3\overset{-}{Cl}$$

In these equations, the coefficients multiply the charges, as well as the radicals bearing the charges, and it will be seen that the numbers of + and − charges produced by each dissociation are equal. Hence, **univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence.** This is an inevitable inference from the electrical neutrality of all solutions. It is confirmed by actual measurement.

To show that this hypothesis is adequate, we next apply it to the explanation of the phenomena of electrolysis. After that some seeming objections will be discussed.

Application to the Explanation of Electrolysis. — A battery is a machine which maintains two points, its poles, or two wires connected with them, at a constant difference of potential. One cell of a storage battery, for example, maintains a potential difference of two volts. When the wires are joined, directly or indirectly, the poles are immediately discharged, but the cell continuously reproduces the difference in potential by generating fresh electricity. Now the effect of immersing two plates, one of which is kept by the battery at a definite positive potential and the other at a definite negative potential, into a liquid filled with floating multitudes of minute bodies, *already highly charged*, may easily be foreseen.

The figure (Fig. 52) will convey some idea of the behavior of the parts of a system such as we have imagined. The electrodes are marked − and +. The negatively charged plate attracts all the positively charged particles in the vessel, and, although these particles are in continuous and irregular motion, they nevertheless begin, on the whole, to drift toward the plate in question. On the other hand, the negatively charged particles are repelled by this plate and attracted by the positive plate, so that they drift in the opposite direction. Those which are nearest each plate, on coming in contact with it, will have their charges of electricity neutralized by the opposite charge on the plate, turning thereby into the ordinary free forms

of the matter of which they are composed. The continuous removal of the electrical charges of the plates through contact with ions of the opposite charge furnishes occasion for recharging of the plate from the battery, and thus gives rise to a continuous current in each wire. Again, the continuous drifting of positively and negatively charged particles in opposite directions through the liquid, constitutes what, in the view of all external means of observation, appears to be an electrical current in the liquid also. A magnetized needle, for example, which is deflected when brought near to one of the wires of the battery, is influenced in the same way by being brought over the liquid between the electrodes. The illusion, so to speak, of an electric *current* is complete, although in reality it is a *convection* of electricity that is taking place. Furthermore, the quantity of electricity being transported across any section of the whole system is the same as that across any other, whether this section be taken through one of the wires, through the electrolyte, or even through the battery at any point. As fast as the ions are thus annihilated as such, the undissociated molecules (mingled with the ions, but not shown in the figure) dissociate and produce fresh ones, as in all chemical equilibria. Eventually, by continuing the process long enough, if the substances set free are actually deposited and do not go into solution again in any form, the liquid can be *entirely* deprived of the whole of the solute which it contains.

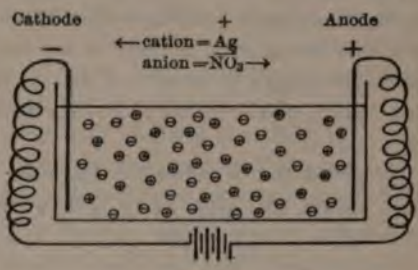


FIG. 52.

The analogy to the transportation of a fluid like water is noticeable, although not complete. Water may be transported in three ways. It may flow through a pipe, it may pass by pouring freely from one container to another, and it may be carried in vessels. Thus a stream of water, essentially continuous, might be arranged, in which part of the passage took place through the pipes, part by pouring from the pipes into buckets, and part by the carrying of those buckets between the ends of the pipes. The quantity of water passing a given point per minute in this system would be the same

at every part, although the actual method by which the water was transported past the various points might be different. In such a disjointed circuit we suppose the electricity to move when carried from a battery through an electrolytic cell. It flows in the wire, passes by discharge between the pole and the ion, and is transported upon the ions in the liquid. The parallel is imperfect, however, because we have used the conception of *two* electric fluids and *because the ions are already charged in the solution, and before any connection with the battery is made.* They do not, so to speak, transport the electricity of the battery, but their own.

Difficulties Presented by this Hypothesis. — The question was raised (p. 207), as to how we can imagine separate atoms of sodium to exist in water without acting upon it, as the metal sodium usually does. But the ions of sodium in sodium chloride solution are *not* metallic sodium. They bear large charges of electricity. They possess an entirely different, and in fact, by measurement, much smaller amount of chemical energy than free sodium. And, as we have seen, the properties of a substance are determined as much by the energy it contains as by the kind of matter. Metallic sodium and ionic sodium are, simply, different substances.

We think of hydrogen chloride and common salt as exceedingly stable substances, and are averse to believing that precisely these compounds should be highly dissociated by mere solution in water. But it must be remembered that in solution they undergo chemical change very easily, and it is only in the dry form that they show unusual stability.

Again, why do not the ions combine, in response to the attractions of their charges? The answer is that they do combine, but the rate at which combination takes place is no greater than that at which the molecules decompose, so that on the whole the proportion of ions to molecules remains unchanged.

Finally, it might appear that the assumption that bodies could retain high charges in the midst of water is contrary to all experience. It must be remembered, however, that the molecular, pure water, which separates the ions from one another, is a perfect nonconductor. The moisture which covers electrical apparatus and causes leakage of static electricity is not pure water, but a dilute solution containing carbonic acid (p. 77) and materials from the glass of which the

apparatus is made. It conducts away the charge electrolytically, by means of the ions it contains, and not by itself acting as a conductor.

Resume and Nomenclature. — The dissociation of molecules into ions is named **ionization.** The substances of the three classes which alone are ionized may be designated **ionogens.** An **ion** may be **defined** as, a molecule bearing negative or positive charges of electricity in proportion to its valence, and formed through the dissociation of an ionogen by a solvent like water.

Each molecule of the solute gives two kinds of ions with opposite charges. These two are forthwith distinct and independent substances, save that the attractions of the charges prevent separation by diffusion. They differ from non-ionic substances of the same material composition when such are known. The electrical charge is one of the essential constituents, and when it is removed the properties alter entirely. Thus we have two kinds of hydrogen, gaseous molecular hydrogen (H_2), and ionic hydrogen ($\overset{+}{H}$), with entirely different chemical properties (p. 208).

The radicals and their chemical behavior are real, and all the peculiarities of aqueous solutions of acids, bases, and salts are experimental facts. Ions, however, like corpuscles, atoms, and molecules, are part of our great system of formulative hypotheses and are added to it in order to maintain its self-consistency. Molecules are units which are not commonly disintegrated by vaporization (p. 87); ions, those which are not commonly disintegrated in double decomposition in solution; atoms, those which are not commonly disintegrated in any chemical action. The ionic hypothesis was first suggested by Svante Arrhenius, a Swedish chemist, in 1887.

Since the writing of the + and − charges over the symbols occupies much space, we shall hereafter employ a dot for the former and a little dash for the latter: $H^{\cdot}$, Cl', $Cu^{\cdot\cdot}$, SO_4'', $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $NH^{\cdot}_4$. In the ions formed from one molecule, the number of dots and dashes must be equal.

Since ionic hydrogen, ionic chlorine, etc., are entirely different in physical and chemical properties from the corresponding free elements, they should receive separate **names.** When it is inconvenient to say "ionic hydrogen," "ionic nitrate radical" (NO_3'), etc., the following will be used:

Symbol.	Name.	Anion of	Symbol.	Name.	Cation of Salts of
SO_4''	Sulphate-ion	Sulphates	$Na^{\cdot}$	Sodium-ion	Sodium
Cl'	Chloride-ion	Chlorides	$Fe^{\cdot\cdot\cdot}$	Ferric-ion	Ferric iron
HSO_4'	Hydrosulphate-ion	Bisulphates	$NH_4^{\cdot}$	Ammonium-ion	Ammonium
OH'	Hydroxide-ion	Hydroxides (bases)	$Fe^{\cdot\cdot}$	Ferrous-ion	Ferrous iron
			$H^{\cdot}$	Hydrogen-ion	Hydrogen (acids)

In using these terms, note that sodium-ion (with the hyphen) is the name of the substance, and not of the hypothetical, charged atom. When speaking in terms of hypothesis, therefore, we may not say "a sodium-ion," any more than we should say "an ionic sodium" or "ionic sodiums." To describe the charged molecule, we must write "a sodium ion," "sodium ions," "chlorate ions," etc.

Faraday distinguished the two kinds of material which proceed with and against the positive current by name. His terminology is still used. Ions which proceed in the same direction as the positive current (Fig. 52) are called **cations** (Gk. κατά, down). Such are $H^{\cdot}$, $Cu^{\cdot\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$. They are **metallic elements**, or groups which play the part of a metal. The electrode (Gk., ὁδός, a path) upon which they are deposited, the negative electrode, is spoken of as the **cathode** (Gk. ἡ κάθοδος, the way down).

The particles which move in the direction of the negative current, and against that of the positive, are named **anions** (Gk. ἀνά, up). The ions Cl', NO_3', SO_4'', MnO_4' are of this kind. They are usually composed of **non-metals**, although sometimes, as in MnO_4', the components may be partially metallic. They are set free at the positive electrode, which is therefore named the **anode** (Gk. ἡ ἄνοδος, the way up). Chemists speak of metals and non-metals as **positive** and **negative elements**, respectively (*cf.* p. 82), even when electrical relations are not directly in question, and ions are not concerned.

Applications: Ionic Equilibrium. — Since the ions are chemically different from their parent molecules, their formation represents a variety of chemical change. The change does not involve any chemical interaction with the water. It is simply a dissociation, *i.e.* reversible decomposition of the dissolved substance.

From the fact that the proportion of molecules ionized is shown to

become greater as more and more of the solvent is added (p. 206), and that removal of the solvent diminishes the proportion of ions to molecules, and finally leaves us the substance entirely restored to the molecular condition, we know that this is a reversible action and therefore a true dissociation. The molecules and their ions adjust themselves like the constituents in any case of chemical equilibrium (pp. 174–180):

$$NaCl \rightleftarrows Na^{\cdot} + Cl'.$$

The chemical behavior of substances in ionic equilibrium will be discussed in the next chapter (see p. 234).

* The mode of formulation previously used (p. 180) may be

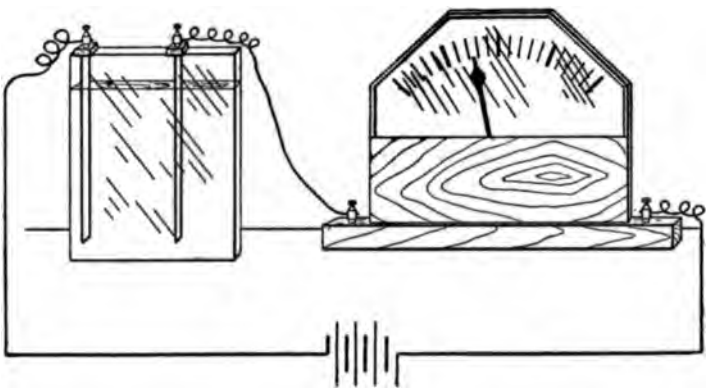


FIG. 53.

employed here. If [NaCl], [Na˙], and [Cl′] stand for the molecular concentrations (numbers of moles per liter) at equilibrium of the molecules, and the two ions, respectively, we have an equilibrium constant (*cf.* p. 181), in this case called the **ionization constant**:

$$K = \frac{[Na^{\cdot}] \times [Cl']}{[NaCl]}$$

When we dissolve a single substance which gives only two ions, the molecular concentrations of the ions are necessarily equal. When some other ionogen with a common ion is present, however, the values of [Na˙] and [Cl′] will be different.

* This paragraph is not required for understanding anything that immediately follows (see Chap. xxxiv).

Applications: To the Interpretation of Conductivity Measurements. — We have seen that when the solution of an ionogen is diluted, the proportion of ions to undissociated molecules increases, while removal of a part of the solvent has the opposite effect (p. 224). Now, a change in the number of ions naturally modifies the capacity of the liquid for carrying electricity, so that observation of the changes in the conductivity of a solution, when the concentration is altered, supplies the simplest means of studying the phenomena of ionization.

A glass trough and amperemeter * (Fig. 53) may be used to illustrate this principle. The electrodes are long strips of copper foil, which pass down at the ends of the trough. After placing the two instruments in circuit with a source of electricity, we first pour very pure water into the cell. With this arrangement, the amperemeter does not indicate the passage of any current of electricity. Concentrated (36%) hydrochloric acid is next cautiously added through a long-stemmed dropping funnel, so that it forms a shallow layer below the water, and the funnel is withdrawn. The situation at this stage is that a definite amount of hydrogen chloride dissolved in a *small* amount of water fills what was before a gap in the electric circuit. The deflection of the needle in the amperemeter indicates that a certain current of electricity is able to pass through this acid. When we now stir the surface of the acid very gently with a thin glass rod, the amperemeter instantly responds, showing an increase in conductivity. As we stir, the conductivity increases, and the increase ceases only when the liquid has become homogeneous. Introduction of an additional supply of water will improve the conductivity still more, but the effect becomes less and less, until no change on farther dilution is perceptible. Reasoning about these effects, we perceive that the amount of hydrochloric acid has not altered during the experiment. Yet the quantity of conducting material between the electrodes must have become greater, for the carrying power of the whole has improved. We were therefore observing the progress of a chemical change of the nonconducting hydrogen chloride into a conducting material. In terms of the hypothesis, hydrogen chloride molecules do not carry electricity

* An amperemeter of low resistance, 0.5–1 ohm, must be used. The current (direct,) passing from the dynamo through one (or two) 32-candle lamps, after being reduced to 8–10 volts by means of a suitable shunt, may be employed.

(p. 214), but the hydrogen and the chloride ions into which it was gradually altered by chemical change do. Furthermore, the change practically ceased at great dilution, for the dissociation into ions was then practically complete. If we could conveniently have started with only liquefied, dry hydrogen chloride in the cell, we should have observed the whole range of changes from zero to the maximum.

When a saturated solution of cupric chloride is used instead of hydrochloric acid, dilution is accompanied by a similar improvement in conductivity. Here we notice, besides, that the yellowish-green liquid, with which we start, changes to a pale blue, as the yellowish-brown molecules of cupric chloride are dissociated and the color of the solution becomes more exclusively that of the copper ions. When the solution has become perfectly blue, further dilution is seen to affect the conductivity but slightly.

Reasoning still further about these phenomena we see that, if we start with a fixed amount of a given substance, the conductivities at different stages of the dilution *must be proportional to the numbers of ions*, and the maximum conductivity attainable by great dilution must represent the effect when *the whole material has become ionic.* Thus, if the conductivity at the maximum is represented, say, by 5, then at the dilution where the conductivity is 2, the proportion of the whole which is ionized is 2/5. When the conductivity becomes 4, 4/5 of the molecules are dissociated and the degree of ionization is .8. When the conductivity becomes 5, 5/5, or all, of the molecules are dissociated. For example, in hydrochloric acid, if we take the normal solution (p. 99) containing 36.5 g. of acid per liter as the unit of concentration, the fractions ionized at various concentrations are as follows: $10N$, 0.17; N, 0.78; $N/10$, 0.91; $N/100$, 0.96. Thus, measurements of conductivity enable us to study the ionic decomposition of all ionogens, and to state accurately the fraction ionized, at each concentration, in solutions of every ionogen. This information is obviously most valuable, for it places us in a position to know the exact constitution of every solution we use in the laboratory. In the following section the data on which such knowledge can be based is given. In the next chapter the mode of applying the data is explained.

Constitution of Solutions of Ionogens: Fractions Ionized.— The **dilute acids** used in the laboratory are generally of six times

normal (6.N) concentration. But often we add only a drop or two to a large bulk of liquid, so that the acids are commonly very dilute as actually employed. The solutions of salts are of different strengths, but the great majority are of normal (.N), or even smaller concentration. In practice they, also, are still further considerably diluted before use. If, therefore, we give the fractions ionized (total molecules = 1) in decinormal solutions (except where otherwise specified), the reader will be able to estimate roughly the proportion of each kind of ions in any application of the reagent. In the case of acids containing more than one displaceable hydrogen unit, the kind of ionization on which the figure is based is indicated by a period. Thus $H.HCO_3$ means that the whole of the ionization is assumed to be into $H^{\cdot}$ and HCO_3'.

FRACTION IONIZED.

Acids.

Nitric acid	0.92	Carbonic acid, $H.HCO_3$	0.0017
Nitric acid (conc., 62%)	0.096	Carbonic acid, $H.HCO_3$ (N/25)	0.0021
Hydrochloric acid	0.91	Hydrogen sulphide, $H.HS$	0.0007
Hydrochloric acid (conc., 35%)	0.136	Boric acid, $H.H_2BO_3$	0.0001
Sulphuric acid, $H.H.SO_4$	0.58	Hydrocyanic acid	0.0001
Sulphuric acid (conc., 95%)	0.01	Permanganic acid (N/2)	0.93
Hydrofluoric acid	0.15	Hydriodic acid (N/2)	0.90
Oxalic acid, $H.HC_2O_4$	0.50	Hydrobromic acid (N/2)	0.90
Tartaric acid, $H.HT$	0.08	Perchloric acid (N/2)	0.88
Acetic acid (N)	0.004	Chloric acid (N/2)	0.88
Acetic acid	0.013	Phosphoric acid, $H.H_2PO_4$	0.26

Bases.

Potassium hydroxide	0.89	Strontium hydroxide (N/64)	0.93
Sodium hydroxide	0.84	Barium hydroxide (N/64)	0.92
Barium hydroxide	0.80	Calcium hydroxide (N/64)	0.90
Lithium hydroxide (N)	0.63	Silver hydroxide (N/1783)	0.39
Ammonium hydroxide	0.014	Water	$0.0_{6}1$
Tetramethylammonium hydroxide (N/16)	0.96		

Salts.

Potassium chloride	0.86	Sodium bicarbonate, $Na.HCO_3$ (N)	(0.52)
Potassium nitrate	0.83	Sodium phosphate, $Na_2.HPO_4$ (N/32)	0.83
Potassium acetate	0.85	Sodium tartrate (N/32)	(0.78)
Potassium sulphate	0.71	Barium chloride	0.76
Potassium carbonate	(0.70)	Calcium sulphate (N/100)	0.63
Potassium chlorate	0.82	Cupric sulphate	0.38
Ammonium chloride	0.85	Silver nitrate	0.81
Sodium chloride (N)	0.67	Zinc sulphate	0.39
Sodium chloride (N/2)	0.73	Zinc chloride	0.73
Sodium chloride	0.84	Mercuric chloride	(<0.01)
Sodium nitrate	0.83	Mercuric cyanide	Minute
Sodium acetate	0.78		
Sodium sulphate	0.69		

In addition to their use in showing the nature of the reagents employed in the laboratory (p. 227), these numbers show also to what extent any pair of ionic substances will unite when mixed (see pp. 233–234), and they likewise indicate the chemical activity of the ionogens when in solution (see next section).

Relation of Ionization to Chemical Activity. — These tables may be used for reference. The import of the following general statements, drawn from the tables, *should be memorized:*

1. **Salts**, with the exception of those of mercury, are all well ionized. In actions involving their ions, salts are therefore **all of the same order of activity**, for a dilute solution of every salt contains a large amount of the ionic components.

2. **Acids** show the most extreme differences in their degrees of ionization. That is to say their solutions must contain very different concentrations of hydrogen-ion. Since their activity as acids depends on this substance (p. 208), and the activity of a substance is proportional to its concentration (p. 180), it follows that **acids will show very great differences in apparent chemical activity**. At this point, therefore, we emerge from semi-physical discussion of the subject and reach something of definite, practical application in chemical work.

The data show that acids may be divided roughly into **four classes** with different degrees of acidic activity:

(*a*) The ionization in decinormal solution exceeds 70 per cent; *e.g.* nitric acid and hydrochloric acid. These are the acids which are chemically most active, for their solutions contain a relatively high concentration of hydrogen-ion.

(*b*) The ionization is between 70 and 10 per cent; *e.g.* sulphuric acid and phosphoric acid. These acids are noticeably less active, for their solutions contain a lower concentration of hydrogen-ion.

(*c*) The ionization is between 10 and 1 per cent; *e.g.* acetic acid. These are the weaker acids, for their solutions contain a very small concentration of hydrogen-ion.

(*d*) The ionization is less than 1 per cent; *e.g.* carbonic and boric acids. These are the feeble acids, for their solutions contain only a minute concentration of hydrogen-ion.

3. The **bases** show **two classes**:

(*a*) Ionization high; *e.g.* potassium hydroxide. These bases are active, for their solutions contain a high concentration of hydroxide-ion.

an acid as a base.

Exercises. — 1. With solutions of the following s
state, (*a*) what will be the products of electrolysis, (*b*) wh
is primary or secondary, and (*c*) how they may be isolat
case: Potassium chlorate, potassium iodide, potassium io
sulphate, sodium peroxide.

2. Make equations (p. 220) showing the ionic and
materials in solutions of potassium bromide, potassium
sodium periodate, aluminium chloride, zinc sulphate.
charges on the ions and give the name of each ionic substan

3. Prepare lists of other anions and cations which
encountered, giving the formula and number of charges of
in each case.

4. If the conductivity of sodium chloride solution at the
is 110, and at greater concentrations is as follows: N,74.4; N
$N/100$, 103, calculate the fraction ionized at each concen

5. If the conductivity of acetic acid solution at the m
352, and at greater concentrations is as follows: $10N$, 0.05
$N/10$, 4.6; $N/100$, 14.3, calculate the fraction ionized
concentration.

6. If 1 c.c. of dilute hydrochloric acid ($6N$) is added
of an aqueous solution, what is the reacting concentrati
acid?

7. Classify all the acids in the table (p. 228) according t

CHAPTER XX

IONIC SUBSTANCES AND THEIR INTERACTIONS

In this chapter, after enumerating the various **classes of ionogens,** and the various **kinds of ionic substances,** we discuss the interactions of the latter. We consider first the relations of the ionic and the molecular substances (in equilibrium) when **a single ionogen** is present, and then take up the ways in which such **an ionic equilibrium is displaced.** Finally we discuss some of the **useful** ionic interactions, in which the equilibria are displaced so far that practically complete interaction occurs: namely, **precipitation, neutralization,** and **displacement.**

The Classes of Ionogens: Mixed Ionogens and Double Salts. — **Acids** are classified according to the number of hydrogen units in their molecules. Thus chloric acid $HClO_3$ is a **monobasic acid,** sulphuric acid H_2SO_4 **a dibasic acid,** and phosphoric acid H_3PO_4 **a tribasic acid.** These terms relate to the fact that, in neutralization (pp. 189, 191) the acids interact with one, two, or three molecules of a base like sodium hydroxide.

Bases are named in a similar way: sodium hydroxide NaOH is a **monoacid base,** calcium hydroxide $Ca(OH)_2$ is a **diacid base.**

Salts like KCl and Na_2CO_3 are **neutral** (see acid salts, below) or **normal salts,** and $NaKCO_3$ and Ca(OCl)Cl (bleaching powder, p. 189) are **mixed salts.**

The most interesting classes of mixed salts are the **acid salts** (p. 171) and the **basic salts.** In acid salts, like $NaHSO_4$ (p. 117) and KH_2PO_4 (p. 118), all the hydrogen of the acid has not been replaced by a metal. In basic salts, like Ca(OH)Cl, part of the basic hydroxyl remains.

There are also many **double salts,** like ferrous-ammonium sulphate $(NH_4)_2SO_4,FeSO_4,6H_2O$, and alum (*q.v.*), some of which are in common use.

All these substances are ionogens (p. 223). The mixed and double salts are, naturally, dissociated into more than two ionic substances.

Hydrogen-ion is a colorless substance. It is sour in ta
presence is recognized by the fact that it turns blue litm
Indicators, below). These properties serve as **tests** fo
they are not interfered with by other ionic substances wh
present. Hydrogen-ion is univalent and, when coml
negative radicals of salts, gives the (molecular) **acids.** T
of acids depends upon the concentration of the hydroge
furnish (pp. 208, 229), and therefore upon their solubili
degree of ionization of the dissolved molecules. Some
little hydrogen-ion that their action on litmus can hardly b

Bases all furnish hydroxide-ion OH′ and some positive
stance (cation), K.OH, NH_4.OH, Zn.$(OH)_2$. Their solut
from those of salts in the constant presence of hydroxide-
the absence of any other anion. The more active bas
those which are soluble and highly dissociated, so that t
high concentration of hydroxide-ion, are called **alkalies.**
potassium and sodium hydroxides. They are often nam
alkalies and, individually, caustic potash and caustic s
solutions are called lyes.

Hydroxide-ion is a colorless substance. Properties whic
tests for bases are that hydroxide-ion possesses a soapy
turns red litmus blue (see Indicators, below). It is univa
combines with positive radicals to form (molecular) bases.

Salts furnish positive and negative ionic substances, whic
either simple or composite, Na.Cl, Na.NO_3, NH_4.Cl,

thought to be present combines to form an insoluble, molecular substance of known color, or appearance, and examine the precipitate if any appears. Thus, when the presence of chloride-ion Cl' is suspected, we may add a solution containing silver-ion $Ag^{\cdot}$, expecting to obtain a precipitate of silver chloride AgCl ($Cl' + Ag^{\cdot} \rightarrow AgCl\downarrow$). In dilute solutions of *salts*, the ions are almost *always* numerous in comparison with the molecules (p. 229), so that salts are practically all active and their solutions almost always respond readily to the tests for the ions they contain. The art of detecting the various ionic substances present in a solution constitutes a large part of the branch of chemistry called qualitative analysis.

All the known ionic substances are found in solutions of salts. The only ions which are not characteristic of salts, although sometimes occurring in their solutions (see acid and basic salts, above), are hydrogen-ion $H^{\cdot}$, and hydroxide-ion OH'.

It will assist the reader if the following facts are kept in mind. The elements which can form a simple positive ion are the **metallic** elements (p. 82, and see Chaps. xxiii and xxxii). Non-metallic elements, like nitrogen, may be present in a positive ion, as in $NH_4^{\cdot}$, but never exclusively. In other words, we know no such substances as nitrogen sulphate, or carbon nitrate. Conversely, the metals are frequently found in the negative ion, but never constitute it exclusively. They are then usually associated with oxygen, as in MnO_4', and Cr_2O_7''.

The Ionic Equilibrium with a Single Ionogen. — In the ionization of a molecular substance, the chemical change is incomplete and the system reaches a condition of equilibrium (p. 225). The action is, therefore, reversible, and there are thus *two routes* to the same equilibrium point. This fact must not be forgotten, for we have to consider the union of ionic substances even more often than the converse change. Now, the **degrees of ionization** of various ionogens **tell us** the location of the equilibrium point, and therefore **the extent of the chemical change** involved in reaching this point by either route, that is, either by the dissociation of molecules or by the union of ions. In a class of interactions, of which all are incomplete, and only those are interesting and useful which approach completeness, we require some means of knowing which are complete and why they are so. The table of fractions ionized (p. 228) supplies most of the required information.

To illustrate, take the case of a single ionogen. When we place hydrogen chloride in decinormal solution, 0.91 of the molecules dissociate. Conversely, when we start with the hydrogen-ion and chloride-ion, say by mixing two solutions each of which contains one of them, then 1 − 0.91, or only 0.09 of these ionic substances will combine.

This exemplifies the case of an active acid. The following equations show the data for six typical substances, namely, two acids, two bases, and two salts:

$$(9\%)HCl \rightleftarrows H^{\cdot} + Cl'(91\%), \quad (98.7\%)HC_2H_3O_2 \rightleftarrows H^{\cdot} + C_2H_3O_2'(1.3\%)$$
$$(11\%)KOH \rightleftarrows K^{\cdot} + OH'(89\%), \quad (98.6\%)NH_4OH \rightleftarrows NH_4^{\cdot} + OH'(1.4\%)$$
$$(16\%)NaCl \rightleftarrows Na^{\cdot} + Cl'(84\%), \quad (62\%)CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''(38\%)$$

These samples are chosen to illustrate, in each pair, the extremes. Thus, with potassium-ion and hydroxide-ion little union takes place, while with ammonium-ion and hydroxide-ion the union is practically complete. In the case of the soluble *salts*, however, there are almost (p. 228) no cases of considerable union of the ions in dilute solutions. The case of water is one of the most extreme:

$$(99.9_5\%)\ H_2O \rightleftarrows H^{\cdot} + OH'\ (0.0_41\%).$$

Hydroxide-ion and hydrogen-ion thus unite almost completely.

Similar reasoning enables us to handle the more complex, but very common case of the mixing of two ionogens. The degrees of ionization tell us the exact condition of each system separately, before mixing. The result of the mixing is best understood by viewing the change as consisting in a *displacement* of each of the equilibria by the action of the components of the other. We consider, therefore, next, the displacement of ionic equilibria.

The Displacement of Ionic Equilibria. — Equilibria are displaced by changes which favor or disfavor one of the opposed actions (p. 177). There may be either, (1) a physical change in the conditions, or a chemical interaction which (2) adds to, or (3) removes one of the interacting substances. Each of these may be illustrated in turn.

As an example of the first, we have the **effect of changing the amount of the solvent** (p. 226). Adding more of the solvent reduces the concentration of the ionic materials and disfavors their union, so that it indirectly promotes dissociation. On the other hand, evaporat-

ing off a part of the solvent favors the encounters of the ions and promotes combination. When the solvent is at last entirely gone, the whole material is molecular (p. 225).

In cases where the ionic and molecular substances are all colorless, these changes can be followed only by a study of the freezing-points or other similar properties of the solutions (p. 206). But when the substances are of different colors, the changes can also be seen. Thus, cupric bromide in the solid form is a jet black, shining, crystalline substance. When treated with a small amount of water it forms a solution which is of a deep reddish-brown tint, giving no hint of resemblance to a solution of any cupric salt. This doubtless represents the color of the molecules. When more water is added, the deep brown gives place gradually to green, and finally to blue. The latter is the color of the cupric-ion ($Cu^{\cdot\cdot}$), and is familiar in all solutions of cupric salts. The colorless nature of solutions of potassium and sodium bromides shows that bromide-ion (Br') is without color. Hence, in the present instance it is invisible. We are thus watching the forward displacement of the equilibrium:

$$CuBr_2 \text{ (brown)} \leftrightarrows Cu^{\cdot\cdot} \text{ (blue)} + 2Br'.$$

If 1 g. of the solid is taken, it dissolves in about its own weight of water, and independent measurement shows that there is relatively little ionization. Hence the solution is deep brown. When 10 c.c. of water has been added, 70 per cent of the salt is ionized, and the solution is green. With 40 c.c. of water, only 19 per cent remains in molecular form, and the blue color of the cupric-ion entirely overbears the tint of the molecules. If we now remove the water by evaporation, all these changes are reversed. When 30 c.c. of the water has been driven off, the solution is green. As the evaporation of the remaining 10 c.c. progresses, the brown color appears. When the water is all gone, the black residue remains. Here we are observing the backward displacement of the equilibrium, $CuBr_2 \leftrightarrows Cu^{\cdot\cdot} + 2Br'$.

2. Cupric bromide may be used to illustrate also the chemical methods of displacing equilibria. Thus, we may show the **effect of adding more of one of the reacting substances.** If, at the green stage, we dissolve solid potassium bromide in the liquid ($KBr \rightleftarrows K^{\cdot} + Br'$), the increased concentration of bromide-ion causes more vigorous interaction of the ions, and the molecules, with their brown color, become prominent again. Adding cupric chloride increases the con-

centration of cupric-ion and has the same effect. In either case, renewed dilution with water reduces the concentrations of all the ions once more, the molecules become fewer, and the brown color is displaced by the blue for the second time.

3. Finally, the displacement of the same equilibrium by removing one of the interacting substances may be illustrated. Thus, if the chocolate-brown solution, in which molecular cupric bromide predominates, is shaken with pulverized lead nitrate (and filtered), two changes are noticed. A pale yellow precipitate of lead bromide appears ($Pb^{\cdot\cdot} + 2Br' \rightarrow PbBr_2$), and the *brown color fades into green.* Here the displacement is the opposite of the last. Instead of reinforcing one of the ions, we have reduced the concentration and in fact almost entirely removed one of them. This has, naturally, stopped the interaction of the $Cu^{\cdot\cdot}$ and Br' which reproduces the brown, molecular $CuBr_2$. Hence the dissociation of the latter has continued to exhaustion of the whole molecular material.

The reader will find that the behavior of these ionic equilibria, and the way in which we discuss and explain it, are complete parallels of the behavior and explanation in the case of ordinary equilibria (pp. 91, 176), which should now be reëxamined. The illustrations in the present section, and particularly the third (*cf.* p. 183), should be considered until every feature is perfectly clear. They furnish the key to understanding the applications which follow. One fact must not escape notice, and that is that in none of the three instances was the forward action (the dissociation) in itself affected. The molecules of cupric bromide have, as we should expect, a certain tendency to decompose. No encounters between these molecules are required for mere decomposition. Hence their decomposition is not influenced by their nearness to, or remoteness from one another (illustration 1), nor by the presence of any other kinds of molecules or ions (illustrations 2 and 3). The effect, whether it involved an apparent increase, or a diminution of the dissociation, *was always accomplished by altering the concentration of the ionic substances, and therefore the activity of the reverse action.*

Applications: Double Decomposition in Solution. — We are now prepared to consider the general case of mixing the solutions of two ionogens.

When solutions of two ionized substances are mixed, the first

reflection which occurs to us is that each of these has been diluted by the water in which the other was dissolved, so that the first effect will be to increase the degree of ionization of both to a certain extent. The next consideration is, however, that we have produced a mixture of four ions, which must have at least some tendency to unite crosswise. Thus potassium chloride and sodium nitrate in dilute solution are very greatly ionized before mixing. The reversible actions, represented by the horizontal pair of the following equations, have taken place extensively. But, by mixing the liquids, we have brought into presence of one another two new pairs of positive and negative ions. Hence, two other reversible actions, the vertical ones,

$$\begin{array}{rcl} KCl & \rightleftarrows & K^{\cdot} + Cl' \\ NaNO_3 & \rightleftarrows & NO_3' + Na^{\cdot} \\ & & \Updownarrow \qquad \Updownarrow \\ & & KNO_3 \quad NaCl \end{array}$$

will be set up and will proceed until a fresh equilibrium of all the ions with all four kinds of molecules has been reached. Thus far the description will fit any case of mixing solutions of two ionogens.

Now, in this particular instance, what is the actual extent of such interaction as has occurred? To answer this question we require to know the proportion of molecules to ions in a solution of each of the four salts. In decinormal solutions it is KCl, 14 : 86; $NaNO_3$, 17 : 83; KNO_3, 17 : 83; NaCl, 16 : 84, so that the salts are all equally well ionized. Furthermore, in a *dilute* mixture, such as we are considering, the *proportions of ions are greater than these figures indicate.* Hence, practically no chemical action has occurred.

That this inference is correct is shown by independent evidence. Thus when the solutions are mixed, no thermal effect is observable. Again, if the solutions are placed in a cell (Fig. 53, p. 225), so that the one forms a layer below the other, no change in conductivity is noticed when the solutions are stirred together. Hence no change in the number of ions has occurred.

We conclude, then, that when two highly ionized substances are mixed, **and the possible products are also highly ionized, soluble substances,** then **practically no chemical action occurs.** This rule applies to all soluble salts (p. 229) and to the highly ionized acids and bases.

Conversely, when two ionized substances are mixed, **an extensive chemical change does ensue in two cases,** namely:

1. When one of the possible products is an insoluble subst **precipitation** occurs, for this removes the ions used in for insoluble body.

2. When one of the possible products, although soluble **ionized**, as in **neutralization**, for this likewise removes the ions to form molecules of the product. We proceed therefore, t these two important classes of actions.

Precipitation. — A typical case of precipitation occu we mix dilute solutions of silver nitrate and sodium chlorid

$$\begin{array}{ccccc} NaCl & \rightleftarrows & Na^{\cdot} & + & Cl' \\ AgNO_3 & \rightleftarrows & NO_3' & + & Ag^{\cdot} \\ & & \Downarrow\Uparrow & & \Downarrow\Uparrow \\ & & NaNO_3 & & AgCl\ (dslvd) \\ & & & & \Downarrow\Uparrow \\ & & & & AgCl\ (solid) \end{array}$$

Here, since the four substances are all *salts*, they are al ionized. If they were all soluble, then, in dilute solutions, 5 per cent of each salt would be in molecules and the rest form. But the *molecules of silver chloride are excessively i* **In all cases of precipitation, we look up the solubilities of the products** (see Table of solubilities inside the front cover). I find that one liter of water will dissolve only 0.0016 g. silver c So the concentration of the AgCl (dslvd) becomes almost zero t precipitation. This displaces the equilibrium, for, the dissc having thus ceased, those of the ions $Ag^{\cdot}$ and Cl' which c are not replaced by others. Hence the silver and chlor disappear. This occurrence affects in turn the equilibria wi and NO_3', so that the NaCl and $AgNO_3$ become completely i Hence the concentrations of NaCl and $AgNO_3$, of $Ag^{\cdot}$ and C of the dissolved AgCl, all become practically zero at last. T tem finally contains only a precipitate of molecular, solid chloride and a solution of the three substances, $Na^{\cdot} + NO_3' \rightleftarrows$ N

The chief change that has as yet befallen the ions of sodium nitrate is that they have been transferred from two separate vessels into one. Potentially the salt has been formed. But the actual union of its ions, to give the second product in the molecular condition:

$$Na^{\cdot} + NO_3' \rightarrow NaNO_3,$$

comes about only when, at some subsequent time, if at all, the water is evaporated away.

The foregoing formulation and explanation apply to every case of mixing ionogens where precipitation occurs, that is, where the products are insoluble acids, bases, or salts.

Neutralization. — We may now consider the case of **mixing solutions of two ionogens** where one is **an acid** and one **a base.**

The general plan of all interactions of acids and bases is as follows:

$$\begin{array}{ccccc} HCl & \leftrightharpoons & Cl' & + & H^{\cdot} \\ NaOH & \leftrightharpoons & Na^{\cdot} & + & OH' \\ & & \Updownarrow & & \Updownarrow \\ & & NaCl & & H_2O \end{array}$$

The ionization of the hydrochloric acid reaches 0.91 in a decinormal solution, and goes further when the acid is diluted with the water of another solution. That of the sodium hydroxide similarly goes beyond 0.84. Thus the substances in the solutions before mixing are almost entirely ionic. The crosswise union, $H^{\cdot} + OH' \leftrightharpoons H_2O$, however, is all but complete, for water is hardly ionized at all (p. 228). The materials on whose interaction with the Cl' and $Na^{\cdot}$, respectively, the maintenance of molecules HCl and NaOH depends, being thus removed, the dissociation of the acid and base promptly brings itself to completion, and the left sides of the equations vanish. Practically all the hydrogen-ion and hydroxide-ion become water, which thenceforth is simply a part of the solvent. The Cl' and $Na^{\cdot}$, however, if the solution is now 1/20 normal, unite to the extent of 0.13 only. If it is more dilute, this union forms a still smaller factor in the whole change. Practically it is negligible. Now all that has been said of *this* acid and base will apply *mutatis mutandis* whenever any active, highly ionized acid and base come together. Thus we may write **one simple equation for all neutralizations of active acids and bases:**

$$H^{\cdot} + OH' \rightarrow H_2O,$$

without omitting anything essential.

neutralization applied to the operation of mixing an acid
Specifically, the absence of effect upon litmus demo
absence of hydrogen-ion $H^{\cdot}$ and of hydroxide-ion OH',
product, and confirms the theory.

Again, a considerable thermal effect accompanies ne
But, in the cases we are discussing, that is where activ
acids are employed, the heat liberated by use of equival
(p. 99) is always the same, namely 13,700 cal. That
the same confirms our theory, for practically the whol
always the formation of 18 g. of water from the ions.

Still again, when we place the acid and base in the c
p. 225), so that the one forms a layer beneath the other,
the amperemeter while we mix the solutions, a marked
the current passing through the cell is noticed. This al
our theory, for it is our belief that one-half of the ions,
$H^{\cdot}$ and OH', disappear as such during the action.

When less highly ionized acids or bases are used, the onl
is that there are more of the molecular materials present
solutions are mixed. But the removal of the $H^{\cdot}$ and OH
mits the molecules of the acid and base to dissociate,
final products are water and the ions of a salt, as before

The foregoing formulation and explanation apply to ev
mixing ionogens, where a very slightly ionized substanc
the products, that is, when water, or a feeble acid, or a
(pp. 229–230) is formed

a solution of an alkali of *known concentration.* The volume of the latter which is required for the purpose is observed. If the alkali is sodium hydroxide, the action taking place is:

$$HCl + NaOH \rightarrow H_2O + NaCl.$$

The volume of acid is measured out into a beaker by means of a pipette (Fig. 54) of fixed capacity, which is filled by suction to the mark on the stem. Suppose the amount to be 25 c.c. The standard alkali solution is placed in a burette (Fig. 55), which is filled down to the tip of the nozzle. A few drops of litmus solution are now added to the acid, and the alkali is allowed to run in slowly. After a time, the hydroxide-ion which this introduces will begin to produce a blue color, close to where the stream enters the liquid. This is at first dissipated by stirring, and the whole remains red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate between blue and red. With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected.

FIG. 54.

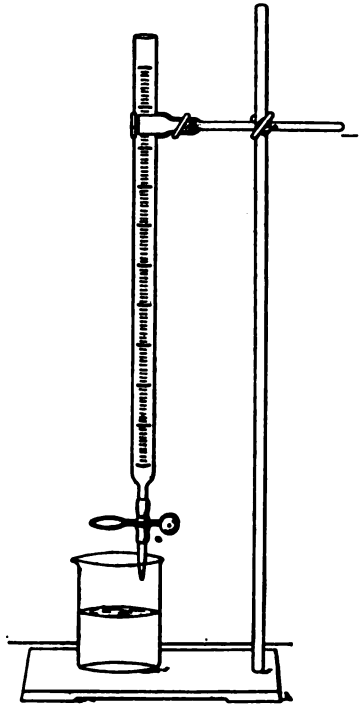


FIG. 55.

By the use of a standard solution of an acid, the quantity of a base may be determined in the same way.

The **standard solutions** used in this work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the

great rapidity. The calculation of the result is also simple.
of normal alkali contains 17 g. of available hydroxyl, and
normal acid, 1 g. of available hydrogen (p. 99). Equa
of normal solutions will therefore exactly neutralize on
18 g. of water being formed by interaction of a liter of eac
the neutralization of the 25 c.c. of hydrochloric acid used
c.c. of normal alkali are required, the acid is twice-nor
When 15 c.c. are required, the acid is $\frac{15}{25}$ or $\frac{3}{5}$ N. If the act
of the acid in the latter case has to be calculated, we reme
there are 36.45 g. of hydrogen chloride in 1 l. of a norma
and therefore $36.45 \times \frac{3}{5} \times \frac{25}{1000}$ g. = .5467 g. in 25 c.c. of
which is $\frac{3}{5}$-normal.

Methods of quantitative analysis in which standard sol
employed are known as volumetric methods, and are muc
analysts and investigators. They occupy much less time t
metric operations, in which numerous weighings have to
and are often just as accurate. The substances, like litmus,
change of color the completeness of the action is made k
called indicators (see below).

Indicators. — Indicators are substances which, in pr
certain other substances, assume a very deep color, or chang
from one deep color to another. Thus, phenolphthaleïn is
in presence of acids (*i.e.*, hydrogen-ion), and red (when dil
in presence of alkalies (*i.e.*, hydroxide-ion). Litmus, aga

and in neutral or acid solutions is, therefore, without visible color. When a base is added gradually to an acid containing some of this indicator, the acid is first neutralized. Then, and not till then, the slightest excess of hydroxide-ion unites with the trace of hydrogen-ion from the phenolphthaleïn, the above equilibrium is displaced forwards, and a visible amount of the red negative ion is formed:

$$\begin{array}{lll} C_{14}H_{10}O_4 \text{ (colorless)} & \rightleftharpoons C_{14}H_9O_4' \text{ (red)} & + \ H^{\cdot} \\ NaOH & \rightleftharpoons Na^{\cdot} & + \ OH' \end{array} \Big\} \rightleftharpoons H_2O.$$

Litmus is a natural dyestuff of unknown chemical structure. One of its colors is that of the molecule, and the other that of the ion.

Methyl orange, $(CH_3)_2NC_6H_4.N : N.C_6H_4SO_3Na$, is a complex organic compound which gives, in acid solution, a red, and in alkaline solution a yellow color.

Congo red is the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions it is red; with acids it turns blue. Paper dipped in Congo red differs from litmus paper in that it shows gradations in color, the blue being much more distinct with an active acid than with a relatively weak one like acetic acid (p. 229). Litmus paper is equally red with all acids save the very feeblest.

Displacement: The Electromotive Series.— In the preceding sections we have dealt with cases in which ionic substances **underwent combination or ionogens dissociated.** This is one of **five kinds of ionic chemical change.** Of the remaining four, ionic **displacement** is the one* that we have most frequently encountered. Thus, certain metals displace hydrogen from dilute acids (p. 66):

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

These interactions do not occur in the absence of water (p. 65), and now appear in a new light, namely, as ionic actions:

$$Zn + 2H^{\cdot} + SO_4'' \rightarrow Zn^{\cdot\cdot} + H_2 + SO_4''.$$

The molecular sulphuric acid and zinc sulphate, which are small in amount, are omitted because they do not take part in the change. On looking at the equation, we perceive that the sulphate-ion is also unaltered by the action, and may be left out likewise:

$$Zn + 2H^{\cdot} \rightarrow Zn^{\cdot\cdot} + H_2.$$

* The **discharge of an ion** and liberation of its material in **electrolysis** (pp. 64, 109, 215) is another. Attention will be called to the remaining two when suitable illustrations occur (see pp. 253, 412).

zinc, give hydrogen faster than do inactive acids (p. former provide a higher concentration (p. 229) of hy that is, of the real interacting substance, than do the la

A similar displacement of negative ions has been met wi 164). Thus, chlorine displaces bromine from solutions bromide-ion.

$$Cl_2 + 2Br' \rightarrow 2Cl' + Br_2.$$

Displacement occurs with all positive ions. Thus, zi place other metallic elements, such as iron, lead, copper, from the ionic conditions, when it is placed in solutions of

$$Zn + Cu^{\cdot\cdot} \rightarrow Zn^{\cdot\cdot} + Cu.$$

Here the copper appears as a red precipitate. Lead, ir displace copper and silver, but not zinc or iron. Copper w silver. Thus the metals can be set down in an order, sucl metal displaces those following it in the list and is displace preceding it. This list (see next page) is known as the el series of the metals, because in electrolysis of normal s their salts, the electromotive force of the current required each metal is less than that for the metal preceding in the present purposes, the list shows the metals in the order of tendency to enter the ionic from the elementary condition.

The electromotive series embodies many facts in the b the metals, and should be kept in mind as furnishing a actions in which a *free metal* is used or produced. For ex

by heating alone. The relations of the metals in respect to combination with elements other than oxygen are similarly expressed by the arrangement in this table.

ELECTROMOTIVE SERIES OF THE METALS.

Alkali metals (*q.v.*)
Alkaline earth metals (*q.v.*)
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Arsenic
Copper
Antimony
Bismuth
Mercury
Silver
Palladium
Platinum
Gold

The position of hydrogen is particularly significant. It will be noted that none of the metals preceding hydrogen are found free in nature as ordinary minerals, while all of the metals succeeding hydrogen, although occurring to some extent in combination, are found also free. The explanation of this is that, by prolonged action upon ordinary water, containing, as it must, carbonic acid and other sources of hydrogen ions, the metals preceding hydrogen must eventually displace hydrogen-ion and pass into some form of combination. The metals following hydrogen do not displace hydrogen-ion and are therefore much less affected by the agencies which are most active in the chemical transformation of minerals. Hence they often remain in the free state.

The negative ions can be arranged in order in a similar way.

To avoid a common misconception, it must be noted that the electromotive series cannot be used to explain the tendency of one radical to dislodge another in double decompositions. The place of an element in the E.M. series defines its relative activity *when free*, and has to do only with actions where *one free element displaces* (p. 68) another. The influences which determine a double decomposition (*cf.* pp. 184, 187) are such as the insolubility of a compound. Thus, potassium bromide solution will slowly convert a precipitate of silver chloride into one of silver bromide: $AgCl + KBr \rightarrow AgBr + KCl$. This occurs because silver bromide is the less soluble salt. But *free* bromine never displaces chlorine from binary combination with a metallic element.

Non-Ionic Modes of Forming Ionogens.— While ionogens may always be made by the union of the proper ions, they must nevertheless, in the absence of the solvent, be regarded as chemical

acid (p. 51), hypochlorous acid (p. 191), and many ot
so formed. Hydrogen fluoride, chloride, bromide, ar
all producible by union of the constituent elements.
are formed from others when the latter are heated;
perchloric acid from chloric acid (p. 196).

Bases are formed by the union of oxides of metals
(p. 81).

The dry ways of forming **salts** are very numerous.
are produced by direct union of the elements, as in the
rides (p. 113), sulphides (p. 29), and other simple salts
made by reduction or oxidation from other salts, as pot
ride from potassium chlorate (p. 47), or potassium perc
the latter (p. 196). Often a reducing or an oxidizing a
as in making sodium nitrite (*q.v.*) from the nitrate.
oxygen salts can be obtained by the union of two oxides
carbonate (*q.v.*) from calcium oxide and carbon dioxid
nium salts are formed by combination of ammonia, whi
ionogen, with acids (p. 121).

In manufacturing salts, methods like the above, as w
involving ionic actions, are very commonly used. In ea
cheapest and most easily accessible materials are chose
least expensive operation is selected.

Exercises. — 1. Give, for each of the following, a
i.e. concise description, in terms of experimental facts: a
111, 187, 201), base (pp. 81, 201), salt (p. 187), acid salt,

5. Give a list of all the colorless ionic substances you can think of.

6. Using the table of fractions ionized (p. 228), prepare lists of the pairs of ionic substances which show the greatest, and the least tendency to combine, and state in each case the proportion combining in decinormal solution.

7. In the case of the green solution of cupric bromide (p. 235), explain in detail (p. 179) the effect of the addition of potassium bromide.

8. In the case of the chocolate-brown, concentrated solution of cupric bromide (p. 235), explain in detail what would happen to the system: (*a*) if metallic zinc were to be added (p. 244); (*b*) if hydrogen sulphide gas were to be led into the solution (CuS is insoluble).

9. Formulate, after the models on pp. 237 and 238, and discuss fully: (*a*) the interaction of dilute sulphuric acid and potassium permanganate (p. 213); (*b*) the preparation of chloric acid (p. 195).

10. What is implied by the statements, that peroxides are salts and that hydrogen peroxide is feebly acid (p. 212)?

11. Formulate after the model on p. 238, and discuss fully, the interaction of: (*a*) sodium peroxide and hydrochloric acid (p. 211); (*b*) barium peroxide and sulphuric acid.

12. Can you invent an interaction of two soluble salts in which both products shall be insoluble (see Table of solubilities, inside of front cover)?

13. For the neutralization of 77 c.c. of a certain alkaline solution, 25 c.c. of normal hydrochloric acid are required. What is the normal concentration of the alkali? If the alkali was sodium hydroxide, what weight of the substance was present? If the alkali was barium hydroxide, what weight of it was present?

14. Formulate (p. 243) the actions of iron and of aluminium on dilute hydrochloric acid.

15. Formulate (p. 244) the displacements of iodine by chlorine and by bromine (p. 166).

16. Which metals (p. 245), beside platinum, would be most likely to form suitable electrodes for an electrolytic cell?

17. To which classes of ionic actions do those of iodine on hydrogen sulphide (p. 167), and of magnesium on cold water (p. 66), belong?

18. Give all the different ionic interactions by which, (*a*) acids, (*b*) bases, and (*c*) salts are prepared, with illustrations of each.

CHAPTER XXI

SULPHUR AND HYDROGEN SULPHIDE

Occurrence. — Free sulphur is found in volcanic regions, where it is mixed with gypsum and other minerals and occupies the pores of pumice-stone. Rocky materials accompanying a mineral in this way are called the **matrix**. Here and there non-volcanic deposits, formed by the action of bacteria, have been met with, as in Louisiana and in Germany. There are many minerals, compounds containing sulphur, which are chiefly important, however, on account of their other constituents. Sulphides of metals, such as **pyrite** (FeS_2), copper pyrites ($CuFeS_2$), galena (PbS), zinc-blende (ZnS), and sulphates, like gypsum ($CaSO_4.2H_2O$), barite ($BaSO_4$), and **celestite** ($SrSO_4$), are fairly plentiful. Sulphur is a constituent of albumin and other substances found in the animal body.

Manufacture. — Most sulphur is obtained by the simple process of melting it away from the accompanying volcanic rock at a low temperature. The liquid sulphur is allowed to run into wooden molds, in which it soli lifies in the form of **roll sulphur**. To produce the best quality it is subjected to distillation from earthenware retorts. When the vapor is led into a large brick chamber, it condenses upon the walls and floor in the form of **flowers of sulphur**.

The greater part of the sulphur of commerce comes from Sicily, where, in 1898, 447,000 tons were manufactured against 41,000 tons elsewhere. It is found in Japan, California, Nevada, and Louisiana. Sulphur is popularly known as brimstone.

Physical Properties. — The chief physical peculiarity of sulphur is that, instead of existing in three physical states only, like water, it possesses two familiar and perfectly distinct solid forms and two different liquid states of aggregation.

1. Native sulphur is yellow, has a sp. gr. 2.06 and melts at 114.5°. It is almost insoluble in water, but dissolves freely in carbon disul-

phide (41 parts in 100 at 18°). The crystals of native sulphur, as well as those obtained by evaporating a solution, belong to the rhombic system (Fig. 1, *cf.* p. 6). Roll sulphur is the same substance as these two, although the crystals in their growth have interfered with one another, and the mass is **crystalline**, simply, and not **well crystallized**. This variety is called, from its form, **rhombic sulphur**.

2. When a large mass of melted sulphur solidifies slowly, and the crust is pierced and the remaining liquid poured out before the whole has become solid, the interior is found to be lined with long, transparent needles. This kind of sulphur is nearly colorless and has a sp. gr. 1.96, melts at 119°, and is in all physical respects a different individual from rhombic sulphur. This variety is named, from the system to which its crystals belong, **monoclinic sulphur**.

A substance which has two solid states of aggregation and, therefore, two crystalline *forms*, is said to be **dimorphous** (two-formed).

3. When melted sulphur is heated, it undergoes another change, which is especially noticeable near 160°. The formerly **pale-yellow, mobile liquid** (S_λ) suddenly becomes **dark-brown** in color and so **viscous** (S_μ) that the vessel may be inverted without loss of material. Beyond 260° the viscidity becomes less, and at 445° the liquid boils and passes into sulphur **vapor**.

When ordinary sulphur is boiled and then allowed *slowly* to cool, the product is crystalline and soluble in carbon disulphide, as before. But when sulphur is boiled and then *suddenly chilled* by pouring into cold water, it is at first semi-fluid. After several days this elastic sulphur, as it is called, becomes hard. It is then found to contain rhombic sulphur mixed with a large proportion of another variety of free sulphur. This is almost insoluble in any solvent. Being without crystalline structure, it is called **amorphous** (Gk. ἀ priv., μορφή form) sulphur. Now amorphous bodies (see Glass) are always supercooled liquids, that is, liquids still existing as such at a temperature at which the solid, crystalline form is the stable one. This is simply the brown, viscous sulphur (S_μ) in a supercooled state. It reverts very slowly to the soluble variety, and years are required for the completion of the reversion at room temperature.

Chemical Properties. — At low temperatures and under reduced pressure, the formula of sulphur vapor is S_8. As the temperature is raised, however, the vapor expands very rapidly, and at 800° the

molecular weight is 64.2, and the formula therefore S_2 (p. 146). The formula of dissolved sulphur, as measured by the freezing-poi method (p. 205), is S_8.

Sulphur is an active chemical substance. When finely divide metals, with the exception of gold and platinum (*cf.* p. 245), a rubbed together with powdered sulphur, union takes place and su phides are produced. Sulphur when heated combines with gre vigor with iron (p. 6), copper, and most of the metals. It unite also with many of the non-metals. Thus with oxygen it produc sulphur dioxide (p. 48), and even sulphur trioxide SO_3. It unite also with chlorine directly. When sulphur is treated with oxidizin agents *in presence of water*, no trace of sulphur dioxide (or sulphuro acid) is formed; the only product is sulphuric acid.*

Uses of Sulphur. — Large quantities of crude sulphur a employed for making sulphur dioxide, which is used in the man facture of sulphuric acid, in bleaching feathers, straw, and wool, an in making alkali sulphites for employment in the bleaching industr The manufacture of carbon disulphide consumes a considerabl amount also. The purified sulphur is employed in the manufactu of gunpowder, fireworks, matches, and, by combination with rubbe of vulcanite. Flowers of sulphur is used in vineyards to destro fungi, which it does by virtue of the traces of sulphuric acid it yiel by oxidation.

Hydrogen Sulphide H_2S.

This gas is found dissolved in some mineral waters, which in co sequence are known as sulphur waters. It is produced in the decom position of animal matter containing sulphur, when air is exclude Hence the distinctive odor of rotten eggs is due in part to its presenc

Preparation. — 1. Hydrogen and sulphur do not unite perce tibly in the cold. At 310° almost complete union occurs, but abo 168 hours are required for the attainment of equilibrium.

2. Sulphides of metals, being salts, are acted upon more or le easily by dilute acids (p. 187), and give hydrogen sulphide. Ferro sulphide, the least expensive of those easily affected, is generall used:

$$FeS + 2HCl \rightleftarrows H_2S\uparrow + FeCl_2.$$

* The paragraph on the chemical relations of the element (see end of th chapter) should be read at this point.

For hydrochloric acid we may substitute an aqueous solution of any active, non-oxidizing acid. A Kipp's apparatus (p. 65) is commonly employed. Since ferrous sulphide is but slightly soluble in water, the action proceeds by a rather complex series of equilibria:

$$\text{FeS (solid)} \leftrightarrows \text{FeS (dslvd)} \leftrightarrows \left.\begin{array}{l}\text{Fe}^{\cdot\cdot} + \text{S}'' \\ 2\text{HCl} \leftrightarrows 2\text{Cl}' + 2\text{H}^{\cdot}\end{array}\right\} \leftrightarrows \text{H}_2\text{S (dslvd)} \rightleftarrows \text{H}_2\text{S (gas)}.$$

The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphide-ion S'' than does ferrous sulphide, in spite of the comparative insolubility of the latter. Hence, the S'' formed from the FeS is continuously removed by union with the hydrogen-ion furnished by the acid, $S'' + 2H^{\cdot} \leftrightarrows H_2S$, and all the other equilibria are constantly displaced forwards on this account. The action is therefore, in essence, like neutralization (p. 239).

3. Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide upon concentrated sulphuric acid (p. 166). Even sulphur itself is reduced by dry, gaseous hydrogen iodide:

$$2\text{HI} + \text{S} \rightarrow \text{H}_2\text{S} + \text{I}_2.$$

Physical Properties. — Hydrogen sulphide is a colorless gas with a characteristic odor. When liquefied, it boils at $-60.4°$ (755 mm.), and in solid form melts at $-82.9°$. The solubility in water at 10° is 360 volumes in 100, and becomes less as the temperature is raised. The gas can be driven out completely by boiling the solution (*cf.* p. 120). The gas is very poisonous, one part in two hundred of air being fatal to mammals.

Chemical Properties of Hydrogen Sulphide Gas. — When heated, the gas **dissociates**:

$$\text{H}_2\text{S} \rightleftarrows \text{H}_2 + \text{S}.$$

At 310° the decomposition is slight (*cf.* p. 81), but becomes greater at higher temperatures.

The gas **burns** in air, forming steam and sulphur dioxide. The temperature of the mantle of flame surrounding the gas, as it issues from a jet, being far above 310°, the gas in the interior is dissociated before it meets with any oxygen. Hence a *cold* dish held across the

flame receives a deposit of free sulphur, and a part of the hydrog also escapes unburnt. It may be remarked that dissociation of t kind probably precedes the combustion of most gaseous compou (see Flame).

The metals, down to and including silver in the electromot series, when exposed to the gas, quickly receive a coating of sulph That the gas should thus behave like free sulphur shows its in bility.

This instability is shown also in the fact that it reduces substan such as sulphur dioxide, which are not affected by free hydrogen

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S.$$

This action takes place in the cold, and much more rapidly when gases are moist than when they are dry (p. 114). Native sulphu probably produced by this action, as both of these gases are fou issuing from the ground in volcanic neighborhoods. Sulphur deposited also when hydrogen sulphide undergoes a partial comb tion with a restricted supply of oxygen, $2H_2S + O_2 \rightarrow 2H_2O +$ and its formation in nature is sometimes to be accounted for in t way.

Chemical Properties of the Aqueous Solution of Hydrog Sulphide. — While the gas itself is not an acid, its solution in wa gives a **feeble acid reaction** with litmus, and is sometimes nam sulphydric acid H_2S, Aq. In a $N/10$ aqueous solution, only .0 (0.07 per cent) of the substance is ionized:

$$H_2S \rightleftarrows H^{\cdot} + HS' (\rightleftarrows H^{\cdot} + S'').$$

Some S'' ions are present. But hydrosulphide-ion HS', altho an acid, is less dissociated than is water itself, and the amount sulphide-ion is therefore very small. The salts of hydrosulphide-i such as NaHS (sodium acid sulphide, see next section), give theref neutral solutions. This behavior is the rule with the acid s of feeble dibasic acids (p. 231).

As an acid, the solution of hydrogen sulphide may be neutrali by bases. For the same reason it enters into double decomposit with salts (see next section).

By the action of **oxygen** from the air upon an aqueous solution hydrogen sulphide, the **sulphur** is slowly **displaced** and appears in form of a fine white powder:

$$O_2 + 2H_2S \rightarrow 2S\downarrow + 2H_2O.$$

This is an action similar to the displacement of ionic bromine by free chlorine (p. 244).

The solution of the gas is a **reducing agent**, as its action upon iodine shows (p. 167). So, also, in presence of an acid, it removes oxygen from dichromic acid (produced by the action of an acid upon potassium dichromate):

$$K_2Cr_2O_7 + 2HCl \rightleftarrows H_2Cr_2O_7 + 2KCl \qquad (1)$$
$$H_2Cr_2O_7 + 6HCl \rightarrow 4H_2O + 2CrCl_3(+ 3O) \qquad (2)$$
$$(3O) \quad + 3H_2S \rightarrow 3H_2O + 3S \qquad (3)$$

Adding: $K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3S.$

The first partial equation (*cf.* p. 159) represents the regular interaction of two ionogens, but the second interaction does not take place unless an oxidizable body (here the hydrogen sulphide) is present to take possession of the oxygen which it is capable of delivering (*cf.* p. 213).

The foregoing illustrates a **fourth kind of ionic chemical change** (p. 243), namely that in which **a compound ion is formed or decomposed.** Here dichromate-ion Cr_2O_7'' gives chromic-ion $Cr^{\cdot\cdot\cdot}$ and water. For other illustrations see pp. 67, 115, 192, 195, 198, 213.

Sulphides. — As a di-basic acid (p. 231), hydrogen sulphide gives both acid and neutral (or normal) sulphides, such as NaHS and Na_2S.

The **acid sulphides** are obtained by passing the gas in excess into solutions of soluble bases:

$$H_2S + NaOH \rightarrow H_2O + NaHS,$$

and are *neutral* in reaction. Their negative ion, HS′, is not further dissociated (see preceding section).

By adding to the above mentioned solution an amount of sodium hydroxide equal to that used before, and driving off the water by evaporation, the second unit of hydrogen is displaced, and "neutral" sodium sulphide is formed:

$$NaOH + NaHS \leftrightarrows Na_2S + H_2O\uparrow.$$

This action is wholly reversed when dry sodium sulphide is dissolved in water, the salt being completely **hydrolyzed** (p. 163) to the acid salt:

$$\left.\begin{array}{l} Na_2S \leftrightarrows 2Na^{\cdot} + S'' \\ H_2O \leftrightarrows OH' + H^{\cdot} \end{array}\right\} \leftrightarrows HS'.$$

a "neutral" salt derived from an active base and a weal
lyzed to some extent by water and gives an alkaline so

Many sulphides are insoluble in water, and these m
roughly into three classes:

1. The sulphides of silver, copper, mercury, an
metals are exceedingly insoluble, and, therefore, do not
dilute acids as does ferrous sulphide (p. 251). These
be made by leading hydrogen sulphide into solutions

$$CuSO_4 + H_2S \leftrightarrows CuS\downarrow + H_2SO_4.$$

The acid produced has scarcely any effect upon the
almost no reverse action is observed. In this action the
is the active substance and, by its removal, all the equil
are displaced forwards.

2. The sulphides of iron, zinc, and certain other met
uble in water, but not so much so as the last class. He
decomposed by dilute acids, and the reverse of the
takes place almost completely. These sulphides must
made, either by combination of the elements, or by addi
sulphide to a solution of a salt:

$$FeSO_4 + (NH_4)_2S \leftrightarrows FeS\downarrow + (NH_4)_2SO_4.$$

No acid is produced in this sort of interaction, and the
insolubility of the sulphide of iron or zinc in water
change nearly complete.

The soluble acid sulphides are **oxidized** in aqueous solution by atmospheric oxygen:

$$2NaSH + O_2 \rightarrow 2NaOH + 2S.$$

The sulphur is not precipitated, but combines with the excess of the sulphide, forming polysulphides (see below). Some sodium thiosulphate is produced at the same time.

Polysulphides.— When sulphur is shaken with a solution of a soluble sulphide or acid sulphide, such as sodium sulphide, it dissolves, and evaporation of the solution leaves substances varying in composition from Na_2S_2 to Na_2S_5.

When an acid is poured into sodium polysulphide solution, minute spherules of rhombic sulphur are precipitated:

$$Na_2S_5 + 2HCl \rightarrow 2NaCl + H_2S\uparrow + 4S\downarrow.$$

The Chemical Relations of the Element Sulphur. — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Exercises. — 1. How could the decomposition of hydrogen sulphide at 310° be rendered, (*a*) more complete, (*b*) less complete? Would the percentage decomposed be affected, (*a*) by reducing the pressure, (*b*) by mixing the gas with an indifferent gas?

2. What are the relative volumes of the gases (p. 145) in the action of, (*a*) hydrogen iodide and sulphur, (*b*) hydrogen sulphide and sulphur dioxide?

3. To what classes of ionic actions (p. 243) do the interactions of hydrogen sulphide solution and, (*a*) oxygen (p. 252), (*b*) sodium hydroxide (p. 253), (*c*) iodine (p. 167) belong?

4. Show which actions on the pages referred to on p. 253 illustrate the fourth kind of ionic chemical change, and how they do so.

5. Why is normal sodium sulphide only half hydrolyzed by water?

THE OXIDES AND OXYGEN ACIDS OF SUI

THE only important oxides of sulphur are the **dioxide** **trioxide** SO_3. They are the anhydrides (p. 51) of sul H_2SO_3 and sulphuric acid H_2SO_4.

The Preparation of Sulphur Dioxide SO_2. — W burns in air or oxygen, sulphur dioxide is produced (larger part of the sulphur dioxide used in commerce obtained by the **roasting** (**calcining**) of sulphur ores. P for example, burns when it has been raised to the kindli ture, on account of the large amount of sulphur which it

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2.$$

It should be noted, in passing, that heating and roas cining are distinct processes in chemistry. **Roasting** always assumes the access of the air and employment of **heating**, in the absence of modifying words, assumes the e the chemical indifference of the air.

Sulphur dioxide is also set free by the action of acid phites. Sulphuric acid and a strong solution of sodiu may be used:

$$Na_2SO_3 \leftrightarrows 2Na^{\cdot} + SO_3'' \leftrightarrows H_2SO_3 \leftrightarrows H_2O + SO_2\,(\text{dslvd}) \rightarrow$$

perature. A part of the acid loses oxygen to form water with the hydrogen of another molecule:

$$H_2SO_4 \rightarrow H_2O + SO_2\ (+\ O) \qquad (1)$$
$$(O) + H_2SO_4 + Cu \rightarrow H_2O + CuSO_4 \qquad (2)$$
$$2H_2SO_4 + Cu \rightarrow 2H_2O + SO_2 + CuSO_4$$

Some easily oxidized non-metals, such as carbon and sulphur, act in the same way, $C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + CO_2$.

Physical and Chemical Properties.— Sulphur dioxide is a gas possessing a penetrating and characteristic odor. This is frequently spoken of as the "odor of sulphur," but it should be remembered that sulphur itself has scarcely any smell at all. The weight of the G.M.V. of the gas (65.54 g.) shows it to be more than twice as heavy as air. By means of a freezing mixture of ice and salt, the gas is easily condensed to a transparent mobile fluid, which boils at $-8°$. The solubility of the gas in water is 5000 volumes in 100. The liquid is completely freed from the gas by boiling (*cf.* p. 120).

As regards **chemical properties**, sulphur dioxide is **stable** (p. 81).

It **unites with water** to form sulphurous acid, H_2SO_3. Although the gas itself sometimes receives this name, it is not acid.

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated.** It is therefore still able to combine directly with suitable elements, such as chlorine and oxygen. When it is mixed with chlorine in sunlight, a liquid, **sulphuryl chloride** SO_2Cl_2 is produced.

Liquefied sulphur dioxide is now sold in tin cans, and is employed for bleaching straw, wool, and silk. As a disinfectant it has been displaced to a large extent by formaldehyde.

Preparation of Sulphur Trioxide SO_3. — Although the formation of sulphur trioxide is accompanied by the liberation of much heat, sulphur dioxide and oxygen, even when heated together, unite very slowly. Ozone, however, combines with the former readily.

The interaction of sulphur dioxide and oxygen is hastened by finely divided platinum, which remains itself unchanged and simply acts as a catalytic agent. The "contact process," as this is called, has been rendered available for the commercial manufacture of sulphur trioxide by Knietsch (1901). At 400°, the temperature used, 98–99 per cent of the materials unite. The vaporous product is

condensed by being led into 97–98 per cent sulphuric ac
concentration of the liquid is constantly maintained at its
the regulated influx of water.

Formerly sulphur trioxide was obtained by the ignition
impure ferric sulphate, $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$. It may
prepared by repeated distillation of concentrated sulphuric ac
a powerful drying agent, like phosphoric anhydride.

Physical and Chemical Properties. — Sulphur trioxide
volatile liquid (b.-p. 46°). The crystals, obtained by cooling
at 14.8°. It fumes strongly when exposed to the air, in consequence
of the union of the vapor with moisture and the production of
drops of sulphuric acid. A white crystalline variety, whose
appearance closely resembles asbestos, is the more familiar form
the substance. It has the formula $(SO_3)_x$.

As to chemical properties, the vapor of sulphur trioxide dissociates
into sulphur dioxide and oxygen (400°, 2%; 700°, 40%).

Sulphur trioxide is not itself an acid, but it is the anhydride
sulphuric acid. When placed in water it unites vigorously, with
a hissing noise due to the steam produced by the heat of the

Just as sulphur trioxide unites with water to give hydrogen
phate, so it combines vigorously with many oxides of metals, pro
the corresponding sulphates:

$$H_2O + SO_3 \rightarrow H_2SO_4, \qquad CaO + SO_3 \rightarrow CaSO_4.$$

The union of an oxide of a non-metal with the oxide of a m
this fashion, is a general method of obtaining salts (*cf.* p. 24

Oxygen Acids of Sulphur. — Sulphurous and sulphuric
have been mentioned frequently already. Next to them in
tance come thiosulphuric acid and persulphuric acid. The co
tions of the acids show their relationships:

Hyposulphurous acid,	$H_2S_2O_4$	Thiosulphuric acid,	H_2S
Sulphurous acid,	H_2SO_3	Persulphuric acid,	H_2S
Sulphuric acid,	H_2SO_4		

Thiosulphuric acid (Gk. θεῖον, sulphur) is so named bec
contains one unit of sulphur in place of one of the units of oxy
sulphuric acid. Besides the above we have also the polyt
acids, namely: Dithionic acid $H_2S_2O_6$, trithionic acid $H_2S_3O_6$,
thionic acid $H_2S_4O_6$, and pentathionic acid $H_2S_5O_6$.

Sulphuric Acid H_2SO_4.

though salts of sulphuric acid, such as calcium sulphate, are dingly plentiful in nature, the preparation of the acid by chemiction upon the salts is not practicable. The sulphates, indeed, act with all acids, but the actions are reversible. The comple- of the action by the plan used in making hydrogen chloride 18), involving the removal of the sulphuric acid by distillation, d be difficult on account of the involatility of this acid. It boils 0°; and acids, less volatile still, which might be used to liber- t, do not exist. We are therefore compelled to build up sul- ic acid from its elements.

e union of sulphur dioxide and oxygen by the contact process, combination of the trioxide with water (p. 257), is the best od for making a highly concentrated acid. For obtaining ary "oil of vitriol," however, the "chamber process" is still extensively.

emistry of the Chamber Process. — The gases, the inter- ns of which result in the formation of sulphuric acid, are: water r, sulphur dioxide, nitrous anhydride N_2O_3 (*q.v.*), and oxygen. e are obtained, the first by injection of steam, the second usually e burning of pyrite, the third from nitric acid, and the fourth by ntroduction of air. The gases are thoroughly mixed in large en chambers, and the sulphuric acid forms droplets which fall e floors. In spite of elaborate investigations, instigated by the sive scale upon which the manufacture is carried on and the ense financial interests involved, some uncertainty still exists in d to the precise nature of the chemical changes which take place. rding to Lunge the greater part of the product is formed by two essive actions, the first of which yields a complex compound that composed by excess of water in the second:

$$H_2O + 2SO_2 + N_2O_3 + O_2 \rightarrow 2SO_2 \begin{matrix} \diagup O-H \\ \diagdown O-NO \end{matrix} \qquad (1)$$

group $-NO$, nitrosyl, is found in many compounds. Here, if re displaced by hydrogen, sulphuric acid would result. Hence compound is called *nitrosylsulphuric acid:*

$$2SO_2 \begin{matrix} \diagup O-H \\ \diagdown O-NO \end{matrix} + H_2O \rightleftarrows 2SO_2 \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} + N_2O_3. \qquad (2)$$

The equations (1) and (2) are not partial equations for one ac action, but represent distinct actions which can be carried o separately. In a properly operating plant, indeed, the nitro sulphuric acid is not observed. But when the supply of wate deficient, white "chamber crystals," consisting of this substa collect on the walls.

The explanation of the success of this seemingly roundabo method of getting sulphuric acid is as follows: The direct unio sulphur dioxide and water to form sulphurous acid is rapid, but i action of free oxygen upon the latter, $2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$ exceedingly slow. Reaching sulphuric acid by the use of these changes, although they constitute a direct route to the result, is n feasible in practice. On the other hand, both of the above actio (1) and (2), happen to be much more speedy, and so, by their u more rapid production of the desired substance is secured at t expense of a slight complexity.

The progress of the first action is marked by the disappearance the brown nitrous anhydride, and, on the introduction of water, t completion of the second results in the reproduction of the same su stance. The nitrous anhydride takes part an indefinite number times in these changes and so facilitates the conversion of a la amount of sulphur dioxide, oxygen, and water into sulphuric ac without much impairment of its quantity.

The supply of nitrous anhydride is maintained by the introduct of nitric acid vapor into the chamber. This acid is made from co centrated sulphuric acid and commercial sodium nitrate $NaNO_3$:

$$NaNO_3 + H_2SO_4 \rightleftarrows HNO_3\uparrow + NaHSO_4.$$

On account of the volatility of the nitric acid, a moderate heat sufficient to remove it from admixture with the other substances, a its vapor is swept along with the other gases into the apparat The initial action which the nitric acid undergoes:

$$H_2O + 2SO_2 + 2HNO_3 \rightarrow 2H_2SO_4 + N_2O_3,$$

may be written, to show the anhydride of nitric acid:

$$H_2O + 2SO_2 + H_2O,N_2O_5 \rightarrow 2H_2SO_4 + N_2O_3.$$

The two molecules of water, one actually, the other potential present, with the two molecules of sulphur dioxide, can furnish t

molecules of sulphurous acid (H_2SO_3). The N_2O_5 in passing to the condition N_2O_3 gives up the two units of oxygen required to convert this sulphurous acid into sulphuric acid.

Details of the Chamber Process. — The sulphur dioxide is produced in a row of furnaces *A* (Fig. 56). When good pyrite is used, the ore burns unassisted (p. 256), while impure pyrite and

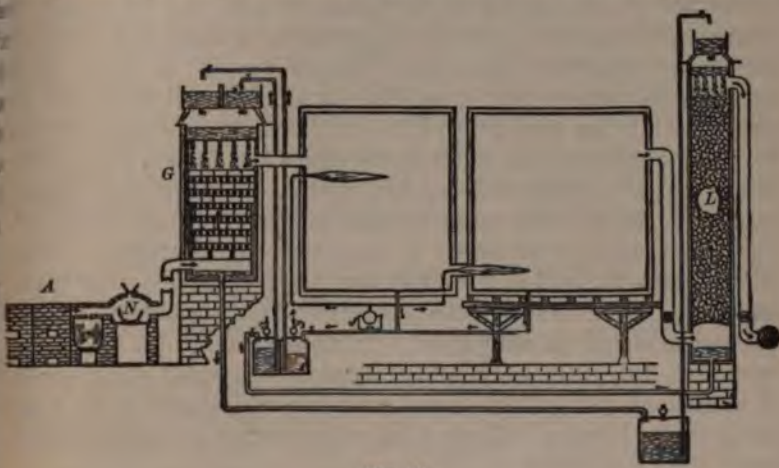


FIG. 56.

zinc-blende ZnS have to be heated artificially to maintain the combustion. The gases from the various furnaces pass into one long dust-flue, in which they are mingled with the proper proportion of air, and deposit oxides of iron and of arsenic, and other materials which they transport mechanically. From this flue they enter the Glover tower *G*, in which they acquire the oxides of nitrogen. Having secured all the necessary constituents, excepting water, the gases next enter the first of the lead chambers, large structures constructed completely of sheet lead. These measure as much as 100 × 40 × 40 feet, and have a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they are thoroughly mixed, and an amount of water considerably in excess of that actually required is injected in the form of steam at various points. The acid, along with the excess of water, condenses and collects upon the floor of the chamber, while the unused gases, chiefly nitrous anhydride

and nitrogen, the latter derived from the air originally admitte find an exit into the Gay-Lussac tower *L*.

This is a tower about fifty feet in height, filled with tiles, ov which concentrated sulphuric acid continually trickles. The obje of this tower, to catch the nitrous anhydride and enable it to b reëmployed in the process, is accomplished by a reversal of actio (2) above. The acid which accumulates in the vessel at the botto of this tower contains the nitrosylsulphuric acid, and by means compressed air is forced through a pipe up to a vessel at the top the Glover tower *G*. When this "nitrous vitriol" is mixed wi dilute sulphuric acid from a neighboring vessel, by allowing both flow down into the tower, the nitrous anhydride is once more set fr by the interaction of the water in the dilute acid (action (2)). Th Glover tower is filled with broken flint or tiles, and the heat gases from the furnace acquire in it their supply of nitrous anhydrid Their high temperature causes a considerable concentration of th diluted sulphuric acid as it trickles downward. The acid, after tra ersing this tower, is sufficiently strong to be used once more for th absorption of nitrous anhydride. To replace the nitrous anhydri inevitably lost, fresh nitric acid is furnished by small open vess *N*, containing sodium nitrate and sulphuric acid, placed in the flu of the pyrite-burners. About 4 kg. of the nitrate are consumed f every 100 kg. of sulphur.

The acid which accumulates upon the floors contains but 60 to per cent of sulphuric acid, and has a specific gravity of 1.5–1.6 The excess of water is used to facilitate the second action. It required also in order that the acid upon the floor may not afterwar absorb and retain the nitrous anhydride, for this substance combin with an acid containing more than 70 per cent of hydrogen sulphat

This crude sulphuric acid is applicable directly in some chemic manufactures, such as the preparation of superphosphates (*q.v* Concentration is effected by evaporation in pans lined with les which are frequently placed over the pyrite-burners in order to econ mize fuel. The evaporation in lead is carried on until a speci gravity 1.7, corresponding to 77 per cent concentration, is reache Up to this point the sulphate of lead formed by the action of th sulphuric acid produces a crust which protects the metal fro further action. When a stronger acid is required, the water driven out by heating the sulphuric acid in vessels of glass or pla

num, or even of cast iron. Commercial sulphuric acid, **oil of vitriol**, has a specific gravity 1.83–1.84, and contains about 93.5 per cent of hydrogen sulphate.

Physical Properties.—Pure hydrogen sulphate has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10°). At 150°–180° the acid begins to fume, giving off sulphur trioxide. When boiled, it yields an acid of constant (p. 120) boiling-point (330°) and constant composition (98.33 per cent). The heat of solution (p. 100) of hydrogen sulphate is very great (39,170 cal.). The solution is thus much more stable (*i.e.*, it contains much less energy) than the pure substance, and hence the latter absorbs water greedily. Many substances containing hydrogen and oxygen are deprived of equivalent amounts of these elements by sulphuric acid. Thus paper, which is largely cellulose $(C_6H_{10}O_5)_x$, and sugar $C_{12}H_{22}O_{11}$ are charred by it, and carbon is set free.

Commercial sulphuric acid is **impure**. It contains, for example, lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination.

Chemical Properties and Uses of Hydrogen Sulphate.—The compound is not exceedingly stable, for dissociation into water and sulphur trioxide begins far below the boiling-point, and is practically complete at 416°, as is shown by the density of the vapor. When raised suddenly to a red heat it is broken up completely into water, sulphur dioxide, and oxygen.

When sulphur trioxide is dissolved in hydrogen sulphate, **disulphuric acid** $H_2S_2O_7$, a solid compound, is obtained. Hydrogen sulphate containing 80 per cent of disulphuric acid is known as "oleum," and is employed in chemical industries. The salts of disulphuric acid may be made by strongly heating the acid sulphates, for example:

$$2NaHSO_4 \rightleftarrows Na_2S_2O_7 + H_2O \uparrow.$$

In view of this mode of preparation by the aid of heat, they are frequently known as **pyrosulphates** (Gk. πῦρ, fire). When they are dissolved in water, the acid sulphates are reproduced.

On account of the large quantity of oxygen which hydrogen sulphate contains, and its instability when heated, it behaves as an **oxidizing agent**. This property has already been illustrated in connection with the action of the acid upon carbon, sulphur, and copper

(p. 257), hydrogen iodide (p. 251), and hydrogen bromide (p. 161 The sulphuric acid is in consequence reduced to sulphur dioxide, an even to free sulphur or hydrogen sulphide. The metals, from th most active down to silver (p. 245), are capable of reducing it, th sulphates being formed. Gold and platinum alone are not attacke Free hydrogen itself is oxidized to water when passed into hydroge sulphate at 160° : $SO_2(OH)_2 + H_2 \rightarrow SO_3 + 2H_2O$.

With salts which it does not oxidize, hydrogen sulphate rea by double decomposition and sets free the corresponding acid. Whe the new acid is volatile, as in the case of hydrogen chloride (p. 117 we are furnished with one of the cheapest means of preparing acid Since hydrogen sulphate is dibasic (p. 231), it forms both acid an neutral salts.

Sulphuric acid is used in almost all chemical industries: for exampl in the Le Blanc process for the manufacture of soda, in the refinin of petroleum, in the manufacture of fertilizers, in the preparation nitroglycerine and gun-cotton, and in the production of coal-t dyes.

Chemical Properties of Aqueous Hydrogen Sulphate. The solution of sulphuric acid H_2SO_4,Aq is a mixture, whose con ponents are: undissociated molecules H_2SO_4, hydrogen-ion H hydrosulphate-ion HSO_4', and sulphate-ion SO_4''. The chemic properties shown by the solution are those of one or other of the components, according to circumstances.

Except in concentrated solutions (normal or stronger) the oxidi ing effects of the undissociated, molecular substance are not encou tered.

The presence of hydrogen-ion is shown by all its usual properti (p. 232).

Sulphate-ion SO_4'', which is found also in solutions of all neutr and acid sulphates, unites with all positive ions. The product, whe insoluble, appears as a precipitate. The introduction of barium ion for example, by adding a solution of barium nitrate or chloride, employed as a test:

$$Ba^{\cdot\cdot} + SO_4'' \rightleftarrows BaSO_4 \downarrow.$$

Since there are other barium salts which are insoluble in water (se Table of solubilities), but no common ones which are not decom posed by acids, dilute nitric acid is first added to the solution suppose

to contain the sulphate-ion. The other ions, if present, then give no precipitate with barium-ion.

Sulphates. — The **acid sulphates**, known also as **bisulphates**, may be produced either by adding to sulphuric acid half an equivalent of a base, and evaporating: $NaOH + H_2SO_4 \leftrightarrows H_2O + NaHSO_4$, or by actions in which another acid is displaced, as in making hydrogen chloride (p. 117). These salts are acid in reaction, as well as in name (*cf.* p. 253), because HSO_4', although a weak, is not a feeble acid. When heated, they yield pyrosulphates (p. 263).

The **neutral** (or normal) **sulphates** are obtained by complete neutralization and evaporation, or by the second of the above methods when a sufficient amount of the salt and a higher temperature are used:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl\uparrow.$$

They may also be made by precipitation, by oxidation of a sulphide at a high temperature, $PbS + 2O_2 \rightarrow PbSO_4$, or by addition of sulphur trioxide to the oxide of a metal (p. 258).

Normal sulphates of the heavy metals decompose at a red heat, some giving off sulphur trioxide (p. 258), others sulphur dioxide and oxygen. The sulphates of the more active metals and of lead, however, are not affected by heating.

Other Acids of Sulphur.

Sulphurous Acid H_2SO_3,Aq. — This term is applied to the solution of sulphur dioxide in water. A portion of the sulphur dioxide remains dissolved physically, while another portion is in combination with the water, forming sulphurous acid. This in turn is ionized, and chiefly, after the manner of the weaker dibasic acids, into two ions, $H^{\cdot}$ and HSO_3'. A little SO_3'' is formed from the latter.

Properties of Sulphurous Acid. — The acid is so **unstable** that it cannot be obtained excepting in solution in water. Chemically it is a comparatively **weak acid**. As a **reducing agent**, it is slowly oxidized by free oxygen, and rapidly by oxidizing agents, turning into sulphuric acid. Thus, when free halogens are added to the solution, sulphuric acid and the hydrogen halide are formed:

$$H_2SO_3 + H_2O + I_2 \rightleftarrows H_2SO_4 + 2HI.$$

addition likewise.

As a **dibasic acid**, sulphurous acid forms **neutral salts** l
and acid salts like $NaHSO_3$.

Sulphites.—The **acid sulphites** of the alkali metals (i.
sium and sodium) are acid in reaction, owing to the appre
ciation of the ion HSO_3'. The sulphites are readily deco
acids giving free sulphurous acid, and the latter partly d
yielding sulphur dioxide.

Calcium bisulphite solution, $Ca(HSO_3)_2$, is used to dissolv
out of wood employed in the manufacture of paper (*q.v.*)

When **heated**, sulphites undergo decomposition. The
being the most stable of all the salts of sulphur acids,
when the salts of any of those acids are decomposed b
The nature of the particular salt determines what othe
shall appear. Here, one molecule of the sulphite furni
atoms of oxygen, sufficient to oxidize three other mole
leaves one molecule of sodium sulphide behind:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4.$$

The sulphites are as readily **oxidized** as is the acid itself.
slowly converted, both in solution and in the solid form, by
ence of the oxygen of the air, into sulphates.

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes:

$$Na_2S_2O_3 + 2HCl \rightleftarrows H_2S_2O_3 + 2NaCl,$$
$$H_2S_2O_3 \leftrightarrows H_2SO_3 + S\downarrow.$$

Persulphuric Acid $H_2S_2O_8$. — This, like the other acids just mentioned, is unstable, and can be kept only in very dilute solution. Its salts, however, are coming into use for commercial purposes and for "reducing" negatives in photography. The salts are prepared by electrolyzing sodium-hydrogen sulphate $NaHSO_4$ in concentrated solution. The persulphuric acid, formed by the union of the negative ions in pairs, as they are discharged on the anode:

$$2\overline{HSO}_4 + 2 \oplus \rightarrow H_2S_2O_8,*$$

undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate crystallizes out. The other salts are made by double decomposition from this one.

Compounds of Sulphur and Chlorine. — When chlorine gas is passed over heated sulphur it is absorbed, and **sulphur monochloride**, a dark reddish-yellow liquid, boiling at 138°, is obtained. The molecular weight of this substance, as shown by the density of its vapor, indicates that it possesses the formula S_2Cl_2. When thrown into water, it is rapidly hydrolyzed, producing suphur dioxide and sulphur: $2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$.

Sulphur itself dissolves very freely in the monochloride, and the solution is employed in vulcanizing rubber.

By the action of sulphur dioxide gas upon phosphorus pentachloride, part of the oxygen in the former is replaced by chlorine:

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3.$$

The products are **thionyl chloride** $SOCl_2$ and phosphorus oxychloride. The former is a colorless liquid, boiling at 78°, and is separated from the latter (b.-p. 107°) by fractional distillation (see Petroleum). It is hydrolyzed by water: $SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$.

Sulphur dioxide and chlorine gases, when exposed to direct sun-

* The signs $\oplus$ and $\ominus$ stand for the (equal) quantities of electricity carried by one equivalent of an ionic substance, and therefore required for its discharge and liberation.

light, unite to form a liquid known as sulphuryl chloride SO_2Cl_2. Ca phor causes the union to take place much more rapidly, owing to its catalytic effect. The compound is a colorless liquid, boiling at 7 With water it gives sulphuric acid and hydrogen chloride:

$$SO_2Cl_2 + 2H_2O \rightarrow SO_2(OH)_2 + 2HCl.$$

Exercises. — 1. What ground is there for assigning the form SO_2 instead of S_2O_4 to sulphur dioxide (p. 257)?

2. Explain why nitric acid is completely displaced by the action sulphuric acid on sodium nitrate (p. 260).

3. What are the relative volumes, (*a*) of sulphur dioxide a nitrogen (p. 145) resulting from the roasting of pyrite (p. 256), of air and sulphur dioxide in making sulphuric acid, (*c*) of nitrog (left) to sulphur dioxide (used) in making sulphuric acid, when py is the source?

4. Make a list of, and classify, the various applications of sulph acid to the liberation of other acids.

5. Formulate the behavior of the hydrosulphate-ion (p. 264) w a solution of barium chloride is added to a rather concentrated s tion of sulphuric acid.

6. Assign to the proper class of ionic actions (pp. 243, 253), the action of iodine on sulphurous acid (p. 265), (*b*) of sulphur sodium sulphite (p. 266), (*c*) the formation of persulphuric (p. 267).

CHAPTER XXIII

SELENIUM AND TELLURIUM: THE PERIODIC SYSTEM

ALONG with sulphur, chemists group two other elements, selenium (Se, at. wt. 79.2) and tellurium (Te, at. wt. 127.6). If the nature of the chief compounds of sulphur is kept in mind, the close analogy between the nature and chemical behavior of the three elements and their corresponding compounds will be noticed at once (see Chemical relations of the sulphur family, below).

Occurrence and Properties of Selenium Se. — Selenium (Gk. σελήνη, the moon) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite (FeS_2). It is found free in the dust-flues of the pyrite-burners of sulphuric acid works. The familiar forms are, the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semi-metallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at 217°. In the latter form it has some capacity for conducting electricity, which is increased by exposure to light in proportion to the intensity of the illumination. It boils at 680°, and at high temperatures has a vapor density corresponding to the formula Se_2.

The element unites directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine.

Compounds of Selenium. — Ferrous selenide, made by heating iron filings with selenium, when treated with concentrated hydrochloric acid gives **hydrogen selenide**:

$$FeSe + 2HCl \rightleftarrows H_2Se\uparrow + FeCl_2.$$

The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of the air (*cf.* p. 262). Other selenides, which, with the exception of

The acid is reduced by sulphurous acid to selenium:
$2H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + Se$.

No **trioxide** is known. **Selenic acid** H_2SeO_4, a white so
by using the most powerful oxidizing agents with selenic
is itself a powerful oxidizing agent, and, even in dilu
liberates chlorine from hydrochloric acid: $H_2SeO_4 + 2HC$
$+ H_2O + Cl_2$. Sulphuric acid (*cf.* p. 263), on the other
oxidizing agent only in somewhat concentrated form, an
it can oxidize hydrobromic acid (p. 161), but not hydro

Tellurium Te. — Tellurium (Lat. *tellus*, the earth)
sylvanite in combination with gold and silver. It is a whi
crystalline substance, melting at 452°. When formed b
tion it is a black powder. The free element unites w
directly, and burns in air to form the dioxide.

The compounds of tellurium are similar in compositio
of preparation to those of selenium. Some differences i
behavior are significant, however. Thus, **tellurious acid**
a very feeble acid and is also somewhat basic, a sulphate (
and a nitrate ($Te_2O_3(OH)NO_3$) being known. In this
differs markedly from sulphurous acid. **Telluric acid** does
indicators, and is therefore actually more feebly acid
hydrogen sulphide. **Tellurium tetrachloride** $TeCl_4$, although h
by water, exists in solution with excess of hydrogen
$TeCl_4 + 3H_2O \rightleftarrows H_2TeO_3 + 4HCl$, showing the tellurious

while their highest valence is found in SO_3, TeO_3, and H_2SeO_4, where they must be sexivalent. The general behavior of corresponding compounds is very similar. At the same time, there is in all cases a progressive change as we proceed from sulphur through selenium to tellurium. The elementary substances themselves, for example, become more like metals, physically, and they show higher and higher melting-points. The affinity for hydrogen decreases, as is shown by the increasing ease with which the compounds H_2X are oxidized in air. The affinity for oxygen likewise decreases, for the elements become increasingly difficult to raise to the highest state of oxidation. On the other hand, the tendency to form higher chlorides becomes greater. We note also that the compounds H_2XO_4 become less and less active as acids, and that a basic tendency begins to assert itself.

The Periodic System.

Classification, or the arrangement of facts on the basis of likeness, is part of the method of science. It is needed to make possible the systematic description of the ascertained facts, and to furnish a guide in investigation, by suggesting relations and so pointing out directions in which new facts of interest may be found. Thus, we have treated the halogens as a group; and chemists, knowing how hypochlorous acid ($HClO$) and perchloric acid ($HClO_4$), and their salts, are made, have been led to attempt to obtain related substances, like HIO and $HBrO_4$ and their salts, by methods suggested by analogy.

Metallic and Non-Metallic Elements. — Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations (p. 116). This distinction we shall continue to employ. **The metallic, or positive elements** (p. 82), (1) form positive radicals and ions containing no other element (*cf.* p. 233). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion together with the ions SO_4'', NO_3', and CO_3''. (2) Their hydroxides, KOH, $Ca(OH)_2$, etc., give the same metallic ion, and the rest of the molecule forms hydroxide-ion. That is to say, their hydroxides are bases and their oxides are basic. The metallic elements often enter *with other elements* into the composition of a negative ion, as is the

ClO_2OH, $P(OH)_5$, $SO_2(OH)_2$, furnish no hydroxyl ions, involve the same consequence. These hydroxides a dissociation, in fact, so that the non-metal forms part o negative radical, and the other ion is hydrogen-ion, ClO_3 $SO_4.H_2$. Their oxides are acidic. (3) Their haloge like PBr_3 (p. 163) and S_2Cl_2 (p. 267), are completely h water, and the actions are not, in general, reversible. of the *typical* metals are not hydrolyzed (see Chap. xx

The distinction is not perfectly sharp, however. Th gives, both salts like the sulphate, $Zn.SO_4$, and chlorid compounds like sodium zincate (p. 67), $ZnO_2.Na_2$.

Classification by Atomic Weights. — Newlands (covered a surprising regularity that became apparent ments were placed in the order of ascending atomic weig hydrogen (at. wt. 1) the first seven were: lithium (7), g boron (11), carbon (12), nitrogen (14), oxygen (16), f These are all of totally different classes, and include forming a strongly basic hydroxide, then a metal of th sort, then five non-metals of increasingly negative chara being the most active non-metal known. The next e fluorine (19) was sodium (23), which brings us back sh elements that form strongly basic hydroxides. Omitti next seven elements were: sodium (23), magnesium (24.4) (27), silicon (28.4), phosphorus (31), sulphur (32), chl

is shown by the fact that the valence and even the physical properties, such as the specific gravity, show a similar fluctuation in each series. In the first two series the compounds with other elements are of the types:

$$LiCl,\ GlCl_2,\ BCl_3,\ CCl_4,\ \begin{cases} N_2O_5 \\ NH_3,\ OH_2,\ FH. \end{cases}$$

$$NaCl,\ MgCl_2,\ AlCl_3,\ SiCl_4,\ \begin{cases} P_2O_5,\ SO_3,\ Cl_2O_7 \\ PH_3,\ SH_2,\ ClH. \end{cases}$$

Thus the valence towards chlorine or hydrogen ascends to four and then reverts to one in each octave. The highest valence, shown in oxygen compounds, ascends from lithium to nitrogen with values one to five, and then fails because compounds are lacking. In the second octave, however, it goes up continuously from one to seven.

Again, the specific gravities of the elements in the second series, using the data for red phosphorus and liquid chlorine, are:

Na 0.97, Mg 1.75, Al 2.67, Si 2.49, P 2.14, S 2.06, Cl 1.33.

Mendelejeff's Scheme. — In 1869 Mendelejeff published an important contribution towards adjusting the difficulty which the elements following chlorine presented, and developed the whole conception so completely that the resulting system of classification has been connected with his name ever since. Almost simultaneously Lothar Meyer made similar suggestions, but did not urge them with the same conviction or elaborate them so fully. The table on the following page, in which the atomic weights are expressed in round numbers, is a modification of one of Mendelejeff's.

The chief change from the arrangement in simple octaves is that the third series, beginning with potassium, is made to furnish material for two octaves, potassium to manganese and copper to bromine, and is called a *long series*. The valences fall in with this plan fairly well. Copper, while usually bivalent, forms also a series of compounds in which it is univalent. Iron, cobalt, and nickel cannot be accommodated in either octave, as their valences are always two or three. At the time Mendelejeff made the table, three places in the third series had to be left blank, as a trivalent element [Sc] was lacking in the first octave, and a trivalent [Ga] and a quadrivalent one [Ge] in the second. These places have since been filled, as we shall presently see. The first two, (the *short*) series have been split in the

ONE OF MENDELEJEFF'S TABLES, MODIFIED.

Li 7	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	Gl 9	B 11	C 12	N 14	O 16	F 19
Na 23	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	Mg 24.4	Al 27	Si 28.4	P 31	S 32	Cl 35.5
K 39	Ca 40	[Sc] 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.6	Zn 65.4	[Ga] 70	[Ge] 72.5	As 75	Se 79.2	Br 80
Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96	... ...	Ru 101.7	Rh 103	Pd 106.5	Ag 108	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.6	I 126.9
Cs 133	Ba 137.4	La 139	Ce 140	Nd 143.6	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...
... ...	... ...	Yb 173	... ...	Ta 181	W 184	... ...	Os 191	Ir 193	Pt 195	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	... ...	... ...
... ...	Ra 226.5	... ...	Th 232.5	... ...	U 238.5	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...	... ...

table, as lithium and sodium closely resemble potassium, while the remaining members of these series fall more naturally over the corresponding elements of the second octave of the third series.

The fourth series (long) is nearly complete. It begins with an active alkali metal, rubidium, and ends with iodine, a halogen. The rule of valence is strictly preserved throughout the series, and in general the elements fall below those which they most closely resemble.

The fifth, sixth, and seventh (long) series are incomplete, but the order of the atomic weights and the valence enable us satisfactorily to place those elements which are known. The chemical relations to elements of the fourth series justify the position assigned to each. Caesium, for example, is the most active of the alkali metals; barium has always been classed with strontium, and bismuth with antimony.

In two cases a slight displacement of the order according to atomic weights is necessary. Cobalt is put before nickel because it resembles iron more closely. Tellurium and iodine are placed in that order to bring them into the sulphur and halogen groups respectively. Their valence and other chemical relations both require this. The general agreement, however, is very remarkable.

General Relations in the System. — In every octave the valence towards oxygen ascends from one to seven, while that towards hydrogen, in the cases of the last four elements (when they combine with hydrogen at all), descends from four to one. The physical properties fluctuate within the limits of each series in a similar way. The values of each physical constant for corresponding members of the successive series do not exactly coincide, however. A progressive change, as we descend each vertical column, is the rule. Thus the specific gravities (water = 1) of the alkali metals rise from lithium (0.53) to caesium (1.87). In the same group the melting-points descend from lithium (186°) to caesium (26.5°).

As yet no exact mathematical relation between the values for any property and the values of the atomic weights has been discovered; only a general relationship can be traced. Anticipating the discovery of some more exact mode of stating the relationship in each case, and remembering that similar values of each property recur periodically, usually at intervals corresponding to the length of an octave or series, the principle which is assumed to underlie the whole, the

elements showing a more or less continuous variation b
limits. Again, the elements at the top are the least me
respective columns. As we descend, the members of ea
more markedly metallic (in the first columns), or, wha
thing, less markedly non-metallic (in the later columns;

In the first series boron is the first non-metal we en
the second series silicon is the first such element. In th
is more difficulty in deciding. Titanium, vanadium, an
are usually, though with questionable propriety, classe
Selenium is undoubtedly a non-metal. Arsenic is, on
non-metal. In the fourth series tellurium is commonl
to be the first non-metal. Thus a zigzag line, shown
separates all the non-metals from the rest of the elemen
fines them in the right-hand upper corner.

A more compact form of the table is printed at the
book, opposite the rear board. The only difference b
and the other is that the two octaves of each long serie
placed in the same set of seven main columns. The iron
and platinum groups occupy a column on the right
columns, and are often called collectively the eighth
newly discovered elements, found chiefly in the air, have
at the left-hand side. Since they do not enter into com
all, their valence may appropriately be given as zero.
exception of argon, the values of their atomic weights agr
this assignment. Hydrogen is the only common elen

have an atomic weight 44 and would be trivalent. From the nature of the surrounding elements, he very cleverly deduced many of the physical and chemical properties of the unknown element and of its compounds. In 1879 Nilson discovered scandium (44), and its behavior corresponded closely with that predicted. Mendelejeff described accurately two other elements, likewise unknown at the time. In 1875 Lecoque de Boisbaudran found gallium, and in 1888 Winkler discovered germanium, and these blanks were filled.

2. By enabling us to decide on the **correct values for the atomic weights** of some elements, when the equivalent weights have been measured, but no volatile compound is known (*cf.* pp. 130 and 147). Thus, the equivalent weight of indium was 38 and, as the element was supposed to be bivalent, it received the atomic weight 76. It was quite out of place near arsenic (75), however, being decidedly a metal. As a trivalent element with the atomic weight 115, it fell between cadmium and tin. Later work fully justified the change. Quite recently, radium (*q.v.*) has been discovered, and found to have the equivalent weight 113.25 and to resemble barium. If, like barium, it is bivalent, it occupies a place under this element, in the last series.

3. By **suggesting problems for investigation.** The periodic system has been of constant service in the course of inorganic research, and has often furnished the original stimulus to such work as well. For example, the atomic weight of tellurium bore the value 128 when the table was first constructed, and it was confidently expected that reëxamination would bring this value below that of iodine (then 127, now 126.97). Several most careful studies of the subject have been made by different methods. It seems probable that the real value of the atomic weight is not far from Te = 127.6, and therefore more than half a unit greater than that of iodine. Since, however, mathematical correspondence is found nowhere in the system, the existence of marked inconsistencies like this need not shake our confidence in its value when it is used with due consideration of the degree of correspondence to be expected.

4. By furnishing a comprehensive **classification of the elements,** arranging them so as to exhibit the relationships among the physical and chemical properties of the elements themselves and of their compounds. Constant use will be made of this property of the table in the succeeding chapters. Having disposed of the halogen and sul-

phur families, situated, respectively, in the seventh and sixth colum of the table (at the end of this book), we shall next take up nitrog and phosphorus from the right side of the fifth column. Then fr the fourth column, we shall select carbon and silicon, and from t third boron, leaving the other, more decidedly metallic elements f later treatment.

Exercises. — 1. Can you explain the presence of *free* selenium the flues of pyrite-burners (p. 270)?

2. How should you attempt to obtain KIO and $KBrO_4$?

3. Make a list of bivalent elements and criticize this method grouping as a means of chemical classification.

4. Write down the symbols of the elements in the fourth ser (that beginning with rubidium, and ending with iodine) on p. 2 Record the valence of each element toward oxygen, using for ref ence the chapters in which the oxygen compounds are described.

CHAPTER XXIV

NITROGEN AND AMMONIA

WHEN the oxygen of the air was removed (p. 45), a gas remained which was largely nitrogen. It did not support combustion or life, and was named *azote* (Gk. ζωτικός, life). The English name records the fact that it is an important constituent of saltpeter KNO_3 (Lat. *nitrum*).

The Chemical Relations of the Element Nitrogen. — In compounds with hydrogen and the metals nitrogen is trivalent, while in those containing oxygen and other negative elements, it is frequently quinquivalent. It is a non-metal, for its oxides are acidic (p. 272). The compounds of nitrogen are often extremely active and interesting. Those of them which we have to discuss in inorganic chemistry are ammonia NH_3 and nitric acid HNO_3, and several related substances.

Occurrence and Preparation. — Free nitrogen is present in the air. The nitrates of potassium and sodium are found in Bengal and Peru respectively. Natural manures, such as guano, contain large quantities of nitrogen compounds, and owe part of their value as fertilizers to this fact. Nitrogen is an essential constituent of vegetable and animal matter. The albumins, for example, contain on an average about 15 per cent of combined nitrogen.

Nitrogen containing about one per cent of argon (*q.v.*) is obtained by burning phosphorus in air, or by passing air over heated copper.

Pure nitrogen is prepared by heating ammonium nitrite:

$$NH_4NO_2 \rightarrow 2H_2O + N_2.$$

In practice, strong solutions of ammonium chloride and sodium nitrite are mixed, a double decomposition results in the formation of ammonium nitrite, $NH_4Cl + NaNO_2 \rightleftarrows NH_4NO_2 + NaCl$, and this breaks up when heat is applied, giving nitrogen.

We may also prepare nitrogen by the oxidation of ammonia (NH_3), by passing the latter over heated cupric oxide (see p. 282), or by the reduction of nitric oxide (NO) by passing this gas over heated copper.

Physical and Chemical Properties. — Nitrogen is a colorless, tasteless, odorless gas, as we should expect from the fact that air possesses these properties. It forms a colorless liquid, boiling at − 194°, and a white solid (m.-p. − 214°). The solubility in water (1.6 vols. in 100) is less than that of oxygen.

The density of the gas shows the formula of free nitrogen to be N_2.

Nitrogen unites with few elements directly. At ordinary temperatures it is almost absolutely indifferent. When passed over heated lithium, calcium, magnesium, or boron, it forms nitrides, in which it is trivalent. These have the formulæ Li_3N, Ca_3N_2, Mg_3N_2, and BN respectively. When the gas is mixed with oxygen or hydrogen, and sparks from an induction coil are passed between platinum wires through the mixtures, small amounts of nitrogen tetroxide N_2O_4 and ammonia NH_3, respectively, are produced.

One case of direct union of nitrogen is of economic importance. The supply required by most plants is obtained from nitrogen compounds contained in fertilizers, or equivalent substances already present in the soil. With the *leguminosæ* (peas, beans, clover, etc.), however, are found associated certain bacteria, which flourish in nodules upon their roots. These bacteria have the power of taking free nitrogen from the air, which penetrates the soil, and producing compounds containing nitrogen. The nodules often contain over five per cent of combined nitrogen. The compounds are chiefly albumins, which are afterwards digested and absorbed by the roots of the plant.

Compounds of Nitrogen and Hydrogen. — The commonest and longest known of these substances is ammonia NH_3, which was first described by Priestley (1774) and named "alkaline air." Curtius discovered hydrazine N_2H_4 in 1889, and hydrazoic acid HN_3 in 1890. Hydroxylamine NH_3O, discovered by Lossen in 1865, is similar to ammonia in chemical behavior.

Ammonia NH_3.

Preparation. — 1. When sparks from an induction coil are passed through a mixture of nitrogen and hydrogen, very small proportions of the materials unite to form ammonia (see below).

2. When water is added to the nitride of magnesium or calcium (p. 280), ammonia is given off and the hydroxide of the metal is formed:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3.$$

3. When parts of animals, particularly the horns, hides, and feathers, which contain complex compounds of carbon, nitrogen, hydrogen, and oxygen, are heated strongly, much of the nitrogen is driven out as ammonia. Hence the name *spirit of hartshorn*, applied to the aqueous solution.

4. The entire commercial supply is obtained as a by-product from operations like the manufacture of illuminating-gas and of coke, in which the destructive distillation of coal takes place. The crude mixture of gases passes first through water, in which most of the ammonia dissolves.

5. In the laboratory, a mixture of slaked lime and some salt of ammonium, such as ammonium chloride, either with or without water, is heated in a flask or retort provided with a delivery tube:

$$Ca(OH)_2 + 2NH_4Cl \leftrightarrows CaCl_2 + 2NH_4OH,$$
$$NH_4OH \leftrightarrows H_2O + NH_3.$$

6. Warming the aqueous solution gives a steady stream of the gas. Since the gas is very soluble in water, it is collected over mercury or by upward displacement of air. It is dried with quicklime.

Physical Properties. — Ammonia is a colorless gas with a pungent, characteristic odor familiar in smelling-salts. The G.M.V. of the gas weighs 17.26 g., so that the density is little more than half that of air (*cf.* p.126). When liquefied it boils at −34° and the solid is white and crystalline (m.-p. − 77°). One volume of water dissolves 1148 volumes of the gas at 0°, 764 volumes at 16°, and 306 volumes at 50°. The 35 per cent solution, sold as "concentrated ammonia," has a sp. gr. 0.882. The whole of the dissolved gas may be removed by boiling (*cf.* p. 120).

Liquefied ammonia is used in **refrigeration**. The gas is liquefied by compression, and the heat which is thus liberated is removed by

flowing water which surrounds the pipes. The liquid then passes into other pipes immersed in calcium chloride brine, and is there allowed to evaporate, the gas returning to the compressor. The heat of vaporization, 260 calories per gram, is taken from the brine, which is thus partially frozen. The resulting freezing mixture of ice and calcium chloride solution is then distributed to the localities to be cooled. The ammonia and brine remain within their respective closed systems of pipes, and are used over and over again.

Chemical Properties. — The discharge from an induction-coil decomposes ammonia (to the extent of 94–98 per cent) into nitrogen and hydrogen. Under the same circumstances, union of the constituents also occurs (up to 2–6 per cent):

$$2NH_3 \leftrightarrows N_2 + 3H_2.$$

Ammonia reduces certain oxides, when led over them:

$$3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2,$$

and burns in pure oxygen with the same result.

Chlorine and bromine combine with the hydrogen and liberate the nitrogen of ammonia. This action may be used for obtaining a stream of nitrogen, provided excess of chlorine is avoided (see Nitrogen trichloride, below). Chlorine is led into a solution of ammonium chloride:

$$2NH_4Cl + 3Cl_2 \rightarrow N_2 \uparrow + 8HCl.$$

The power to form a base by combination with water is the most characteristic property of ammonia:

$$NH_3\,(gas) \leftrightarrows NH_3\,(dslvd) + H_2O \rightleftarrows NH_4OH \leftrightarrows NH_4^{\bullet} + OH'.$$

Probably only a small proportion of the gas is actually combined at any one time, the greater part being simply dissolved.

The gas unites also with acids, forming salts (*cf.* p. 232), which, in solution, are highly ionized:

$$NH_3 + HCl \rightarrow NH_4.Cl,$$
$$NH_3 + HNO_3 \rightarrow NH_4.NO_3.$$

Ammonium Compounds. — Since NH_4 plays the part of a metallic element, entering into the composition of a base and of a series of salts, it is named ammonium. As this radical forms a univ

lent, positive ion and gives a distinctly alkaline base, it is classed with the metallic elements of the alkalies (*q.v.*).

Ammonium hydroxide, although less completely ionized than potassium hydroxide, affects litmus easily. In a normal solution about 0.4 per cent of the ammonia is in the form of ammonium-ion $NH_4^{\cdot}$. When an acid is added to the solution, the correspondingly small amount of hydroxide-ion which exists in it is removed and the various equilibria are displaced forwards. The final result is the same as with any other base:

$$\left.\begin{array}{r} NH_3(\text{dslvd}) + H_2O \rightleftarrows NH_4OH \leftrightarrows NH_4^{\cdot} + OH' \\ HCl \leftrightarrows \quad Cl \quad + \quad H^{\cdot} \end{array}\right\} \leftrightarrows H_2O.$$

When strongly heated, all **ammonium salts** are decomposed and, usually, give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. If the acid is volatile without permanent decomposition, it reunites with the ammonia when the vapor is cooled:

$$NH_4Cl \rightleftarrows HCl + NH_3.$$

The use of ammonium chloride (salammoniac) in **soldering** depends on the dissociation of the salt, by the heat of the iron, and the action of the liberated hydrochloric acid on the oxide which covers the surface of the metal to be soldered.

The **test** for ammonium salts is to warm them, dry or in solution, with a base:

$$\left.\begin{array}{r} (NH_4)_2SO_4 \leftrightarrows SO_4'' + 2NH_4^{\cdot} \\ 2KOH \leftrightarrows 2K^{\cdot} \quad + 2OH' \end{array}\right\} \leftrightarrows 2NH_4OH \rightleftarrows 2H_2O + 2NH_3\uparrow,$$

when the *odor of ammonia* becomes noticeable. When the solution is used, it is the tendency of the $NH_4^{\cdot}$ and OH' to unite to form the slightly ionized molecular hydroxide that sets the other equilibria in motion.

In ammonium salts, the nitrogen is quinquivalent.

Hydrazine N_2H_4. — By reduction of a compound of nitric oxide and potassium sulphite by means of sodium amalgam,* a solution of hydrazine hydrate is obtained:

$$K_2SO_3,2NO + 3H_2 \rightarrow N_2H_4,H_2O + K_2SO_4.$$

* The sodium dissolved in the mercury interacts with the water, giving hydrogen (see Active state of hydrogen).

When the hydrate is distilled with barium oxide, under reduced pressure, hydrazine is liberated:

$$N_2H_4,H_2O + BaO \rightarrow N_2H_4\uparrow + Ba(OH)_2.$$

Hydrazine hydrate freezes at about − 40° and boils at 118.5°. Its aqueous solution is alkaline, and salts are formed by neutralization.

Hydrazoic Acid HN_3. — When nitrous oxide (*q.v.*) is led over sodamide at 200°, water is liberated and sodium hydrazoate remains behind:

$$NH_2Na + N_2O \rightarrow NaN_3 + H_2O.$$

A dilute solution of the free acid is best obtained by distilling the lead salt with dilute sulphuric acid.

The pure acid (b.-p. 37°) is violently explosive, resolving itself into nitrogen and hydrogen with liberation of much heat:

$$HN_3,Aq \rightarrow H + 3N + Aq + 61{,}600 \text{ cal.}$$

Halogen Compounds of Nitrogen. — When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride**, are formed: $3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl$. It is extremely explosive, resolving itself into its constituents with liberation of much heat.

When a solution of iodine in potassium iodide solution (p. 165) is added to aqueous ammonia, a brown precipitate is formed. This seems to have the composition $N_2H_3I_3$, and is named **nitrogen iodide**. It may be handled while wet. When dry, if touched with a feather it decomposes into its constituents with violent explosion.

Exercises. — 1. When moist air is used as a source of nitrogen, what advantage is there in using copper rather than the less expensive metal iron, for removing the oxygen (p. 66)?

2. How many grams of water at 0° could be frozen (p. 78) by the removal of the heat required to evaporate 50 g. of liquid ammonia (p. 282)?

3. How many grams of ammonia are contained in 1 l. of "concentrated ammonia" (p. 281)?

4. What are the ions of hydrazine hydrate? Formulate (p. 239) the neutralization of this base with sulphuric acid.

5. What is the object attained by distilling under reduced pressure in making hydrazine (p. 284)?

6. Classify (pp. 124, 163) the interaction of a nitride with water (p. 281) and of chlorine and ammonium chloride (p. 282), and the results of heating ammonium nitrite (p. 279) and ammonium chloride (p. 283).

CHAPTER XXV

THE ATMOSPHERE. THE HELIUM FAMILY

THE pressure which is exerted by the air upon each square centimeter of the earth's surface is 1033.6 g., or a little over one kilogram. This is nearly fifteen pounds to the square inch.

There are three classes of components in the air. Those of the first class, oxygen, nitrogen, and the inert gases of the helium family (see below), are present in almost constant quantities. Those of the second class are very variable in quantity, although found in all samples of air, and include carbon dioxide and water vapor. Those of the third class, such as the sulphur dioxide in city air, are accidental. Finally, one significant component of the air is the dust.

Components which are Constant in Amount. — In the determination of the oxygen in air, phosphorus in the form of thin wire may be used. In this way a great surface is obtained, and the absorption of oxygen from a measured sample of air may be carried out in a few seconds.

In the air taken from mines, from mountain tops, from the surface of the sea, and from inland regions, the percentages of oxygen by volume are found to be fairly constant, ranging between 20.95 and 21.00, the latter being the proportion in normal air.

When the residual gas is led slowly through a heated tube containing magnesium, the nitrogen unites with the metal to form the solid magnesium nitride (p. 280), and only about 10 c.c. out of every liter remains uncombined. This residuum is argon, mixed with one hundredth of its volume of other gases belonging to the helium family. It is possible that a trace of hydrogen (*cf.* p. 63) is one of the regular components of air.

Components which are Variable in Amount. — Pure country air contains about 3 parts in 10,000 of carbon dioxide. In city air there are from 6 to 7 parts in the same volume, while in the air of audience-rooms the proportion may rise as high as 50 parts.

To determine the proportion of carbon dioxide, a measured olume of air is bubbled slowly through a measured volume of a olution of barium hydroxide of known concentration. Barium carbonate is precipitated: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3\downarrow + H_2O$, and he quantity of barium hydroxide remaining is determined by itration (p. 242).

The sources of the carbon dioxide in the air are numerous. It omes from the decay of vegetable and animal matter, in which, hiefly through the influence of minute vegetable organisms, the arbon is oxidized to carbon dioxide. It is formed also by the combustion of coal and wood, and is exhaled by animals. The proportion of this gas in the air would naturally increase continuously, though slowly, as the result of these processes, were it not that it is removed just as continuously by the action of growing plants (see p. 324).

The quantity of **water vapor** in the air is constantly changing. It increases locally by evaporation from the soil and from natural waters, particularly in warm weather. It decreases when local cooling leads to the precipitation of water in the forms of mist and rain. The phrase commonly heard, that on a moist day the atmosphere is "laden" with moisture, is peculiarly inapt. We recognize at once from observation of the barometer, which is lower in such a state of the atmosphere, that the pressure of the air is less. Moist air must be lighter than dry air, for in it a certain proportion of water molecules, of molecular weight 18, is substituted for an equal number (*cf.* p. 125) of molecules of nitrogen and oxygen whose relative weights are 28 and 32 respectively. The result is therefore a diminution in the specific gravity of the air. The proportion of water in a given volume of air may be measured most accurately by permitting the air to stream slowly through tubes filled with calcium chloride or phosphoric anhydride. The increase in weight of the charged tubes represents the quantity of moisture abstracted from the sample.

The **dust** varies both in kind and quantity according to the locality. It is found to be partly inorganic. The organic dust may be divided into two kinds. The part which is dead includes coal dust, refuse from the streets, minute shreds of cotton, linen, hay, etc. The living dust consists of pollen grains, spores of fungi and other plants, bacteria, and similar microscopic organisms. The presence of microscopic germs in the air is shown by the fact that when nutritive

Flasks can be filled with dustless air through the c
that which they contain by air drawn through a wi
with 12–15 inches of cotton. It has been shown h
dustless air behaves differently from ordinary air in
way in which its moisture condenses. In ordinary
particles act as nuclei, and a fog is formed. In dust
can be produced.

Air a Mixture. — Since the main components o
definitely identified until the end of the eighteenth c
understand why the substance was for long consid
element. The experiments which we have described
oxygen was removed from the air and the nitrogen re
prove that the original constituents were present simp
cal mixture. They might have been combined, and t
of phosphorus, for example, might have represented t
oxygen from combination with nitrogen and its app
the phosphorus. It may be well, therefore, to po
reasons which lead us to regard the air as a mixture:

1. When oxygen and nitrogen are mixed in the prope
we obtain a gas identical with air in all its properties, a
evidence of any production or absorption of heat, s
occur in case of chemical combination.

2. The proportion by volume is not perfectly const

3. The proportions by weight in which the con
contained in air are not integral multiples of the atom

Graham suggested an illustration which will make those proportions clearer. He says that if we imagine the air to be divided by magic into its components, and to remain separated for a time sufficiently long to enable us to note the proportions, and if the substances arrange themselves in the order of their specific gravities, we should have the following layers resting upon the surface of the earth and one upon another: On the earth, five inches of water; above that, thirteen feet of carbon dioxide; above that, a mile of oxygen; and on the top, about four miles of nitrogen. This would be on the assumption that these gases were compressed so as to have the same density throughout. We should now add a layer of argon, of about ninety yards thickness, between the carbon dioxide and oxygen.

Air and Health. — As human beings we have an especial interest in the composition of the air, since our living depends upon the oxygen which we secure by breathing it (*cf.* p. 52). We draw about half a liter of air into our lungs at each breath, or about half a cubic meter per hour. The oxygen of this air is partly used, being taken up by the blood, and part remains in the exhaled air. On the other hand, carbon dioxide is given off in the lungs and passes out with the unused oxygen. The nitrogen is unaffected. In 100 c.c. of expired air there are contained about 15.9 c.c. of oxygen and 4.5 c.c. of carbon dioxide. The total quantity of oxygen consumed during twenty-four hours is about three-fourths of a kilogram, or more than half a cubic meter. While the greater part of this gains access to the body through the lungs, more or less exchange of gases takes place in all animals through the skin. The lower limit of oxygen for respirable air is about 10 per cent, although a candle goes out when the proportion reaches about 18.5 per cent.

Liquefaction of Gases. — The earliest experiments of this kind were made by Northmore (1805), who liquefied chlorine, hydrogen chloride, and sulphur dioxide. In 1823 chlorine was again liquefied by Faraday. During the following years he reduced sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrous oxide, cyanogen, and ammonia to the liquid condition. In 1883 Wroblewski and Olszewski prepared visible amounts of liquid oxygen. About the same time Dewar devised means of manufacturing large quantities of liquid air and oxygen. The most successful apparatus for use on a small scale is that devised by Hampson.

Liquid Air. — Liquid air varies in composition, as the nitrogen (b.-p. − 194°) is less condensible than the oxygen (b.-p. − 182.5°). It boils at about − 190°, and contains about 54 per cent of oxygen by weight, while air contains 23.2 per cent. By allowing evaporation to go on, a liquid containing 75 to 95 per cent of oxygen is easily obtained (*cf.* p. 46). The gas secured by the evaporation of the residue is pumped into cylinders and sold as compressed oxygen. Cartridges made of granular charcoal and cotton waste, when saturated with liquid air, have been used as an explosive in mining.

The Helium Family.

Argon. — Lord Rayleigh was the first to observe that, while specimens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decomposition of five different compounds, such as urea and certain oxides of nitrogen, the results agreed well amongst themselves. The mean weight of a liter of this nitrogen was only 1.2505 g. The difference, amounting to nearly 7 mg., was very much greater than the experimental error. The suspicion naturally arose that some heavier gas was present in natural nitrogen. Soon after (1894), Professor, now Sir William Ramsay obtained argon by removal of the greatly preponderating nitrogen by means of magnesium (p. 280). The new gas had a molecular weight of about 40, and was therefore more than one-third heavier than nitrogen.

The exact density of argon is 39.9. When liquefied it boils at − 186°, and the colorless solid melts at − 189.5°. The solubility of the gas in water (4 volumes in 100) is two and one-half times that of nitrogen. It has not been found to enter into any sort of chemical combination, and was named argon on this account (Gk. ἀργός, inactive). The physical properties show that the molecules of the gas, like those of mercury (p. 138), are monatomic.

Helium. — In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences which was not given by any terrestrial substance then known. The line was so conspicuous that it was attributed to the presence of a new chemical element, which was named **helium** (Gk. ἥλιος, the sun). Ramsay, in searching for

sources of argon, examined the " nitrogen " which was reported by various mineralogists as being disengaged when certain rare minerals were heated. These minerals, cleveite, uraninite, and bröggerite, were chiefly compounds of uranium, yttrium, and thorium. He was surprised to find (1895) that the gas was not always nitrogen. It frequently contained a large proportion of a very light gas, the spectrum of which was identical with that of solar helium. The same gas is found in small amount in the atmosphere. Helium does not exhibit any tendency to enter into combination. It is monatomic and its density shows that its molecular weight is 4. It has neither been liquefied nor solidified.

Neon, Krypton, and Xenon. — When the argon obtained from atmospheric nitrogen is cooled with liquid air (− 185°), the argon, krypton, and xenon are liquefied, and the neon and helium are dissolved by the liquid. When heat is allowed to reach the mixture, the last two gases escape first, along with much argon. When most of the argon has escaped, the krypton and xenon still remain liquid. By repeated liquefaction and fractional evaporation (see under Petroleum), the krypton and xenon are separated from the argon and from one another. When the vessel containing the mixture of helium and neon is immersed in liquid hydrogen (− 240°), the second freezes to a white solid, and the helium, which remains gaseous, can be pumped off.

These gases are all entirely inactive chemically, and are all monatomic. Their molecular weights are: Neon, 20; krypton, 81.5; xenon, 128.

Exercises. — 1. A sample of moist air, confined over water at 15° and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at 0° and 760 mm.?

2. Calculate, from the data on p. 286 and the densities, the percentage by weight of the three principal components of air.

3. Of the proofs that air is a mixture (p. 288), which shows that *no part* of the components is combined, and which that the components are not *wholly* combined?

THE names and formulæ of the oxides and oxyge
are as follows:

Nitrous oxide N_2O	⟵	Hyponitr
Nitric oxide NO		
Nitrous anhydride N_2O_3	⟷	Nitrous a
Nitrogen tetroxide N_2O_4 and NO_2		
Nitric anhydride N_2O_5	⟷	Nitric acid

All the oxides are endothermal compounds (p. 5
exceptions of the third and the last, they are all
The acids, when deprived of the elements of water
opposite which they stand. Conversely, exceptin
nitrous oxide, the anhydrides with water give t
these substances are obtained directly or indirectly f
nitric anhydride by removal of water, the others by
turn, therefore, first, to nitric acid, its sources and

NITRIC ACID HNO_3.

Sources. — Sodium nitrate, or Chili saltpeter, is f
region near the boundary of Chili and Peru. The
5 feet thick, 2 miles wide, 220 miles long, and conta
cent of the salt. Purification is effected by recrystall
sium nitrate, or Bengal saltpeter, is found in the soil
hood of cities in India, Persia, and other oriental cou

Preparation. — When any nitrate is treated with any acid, nitric d is formed by a reversible double decomposition. As sodium rate is the cheapest salt of nitric acid, it is always employed. For ı same reason of low cost, and, above all, because of its relative ·olatility, sulphuric acid is used to displace it:

$$NaNO_3 + H_2SO_4 \leftrightarrows NaHSO_4 + HNO_3\uparrow.$$

e nitric acid is rather volatile (b.-p. 86°), while sulphuric acid (b.-p. ſ°) is much less so, and the two salts are not volatile at all. Thus ı interaction proceeds to completion very easily (*cf.* p. 184). The terials are heated in cast-iron stills, and the vapor is condensed in thenware pipes surrounded by water.

Another action by which attempts are being made to manufacture ric acid is the direct union of the nitrogen and oxygen of the air der the influence of an electric discharge. The nitrogen tetroxide O_2), which is formed in small amounts at a time, is dissolved in ter:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO.$$

e nitric oxide gas, on escaping from the water, unites directly with ·gen to reproduce the tetroxide. The reaction is of interest, indeıdently of this one application, because of its reversibility. It proıds forward with excess of water, while the reverse action takes ce when nitric oxide (*q.v.*) comes in contact with concentrated ric acid in which the quantity of water is at a minimum.

Physical Properties. — Nitric acid is a colorless, mobile liquid, ling at 86°, and freezing to a solid which melts at − 47°. It nes strongly when its vapor issues into moist air (*cf.* p. 120). An ıeous solution containing 68 per cent of the acid boils at 120.5°, ile the pure acid, pure water, and all other mixtures, boil at lower ıperatures. This 68 per cent nitric acid of constant boiling-point 120) forms the " concentrated nitric acid " of commerce.

Chemical Properties. — 1. Like chloric acid (p. 196), and other ·gen acids of the halogens, nitric acid is most stable when mixed h water. The pure (100 per cent) acid **decomposes** while being tilled:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2,$$

not with explosive violence like chloric acid. The distillate is ored brown by dissolved nitrogen tetroxide (NO_2). Repeated

acid and liberates more of the tetroxide than does m

2. Nitric acid, when dissolved in water, is highl is therefore active as an **acid**. By interaction with l oxides it forms nitrates.

3. When pure nitric acid (b.-p. 86°) is poured u anhydride, the latter combines with the elements distillation gives **nitric anhydride**: $2HNO_3 + P_2O_5 \rightarrow N_2$ The anhydride is a white solid melting at 30° and boil unites vigorously with water to form nitric acid. spontaneously into nitrogen tetroxide and oxygen, $2N_2O$

4. Like the unstable oxygen acids of the halogens, n **oxidizing agent** even when diluted with water. The the products into which it may be decomposed by reduc renders separate treatment of this property necessary (

5. Nitric acid interacts energetically with many carbon to give **nitro-derivatives**. Thus, when heated (carbolic acid) it gives **picric acid** (trinitrophenol, HC which crystallizes in yellow needles in the mixture:

$$C_6H_5(OH) + 3HONO_2 \rightarrow C_6H_2(OH)(NO_2)_3 + 3$$

6. Organic compounds of another class, the alcohols act with molecular nitric acid in a different way. mixed with sulphuric acid, which assists in the remov ments of water (p. 263). Thus, when glycerine is add the cooled mixture, glyceryl nitrate (so-called nitro-

Nitrates. — The nitrates are all more or less easily soluble in water. When heated they decompose in one or other of three ways (see pp. 296, 299, 300). The individual nitrates, such as sodium nitrate and potassium nitrate, are described elsewhere.

Nitric Oxide and Nitrogen Tetroxide.

Preparation of Nitric Oxide NO. — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid or of ferrous chloride in hydrochloric acid:

$$\begin{array}{rcll} 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3\ (+\ 2H) & \times\ 3 & (1) \\ (3H) + HNO_3 \rightarrow NO + 2H_2O & \times\ 2 & (2) \\ \hline 6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O. & & \end{array}$$

The first partial equation does not take place at all unless an oxidizing agent like nitric acid is present (p. 213). The multiplication of the two partial equations by 3 and 2 respectively is required in order that the hydrogen, which is not a product, may cancel out. This action may be used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

As we shall see, this gas may also be obtained when sufficiently dilute nitric acid (sp. gr. 1.2) acts upon copper. Although some nitrous oxide and nitrogen are produced in this interaction, it furnishes a convenient method of generating the gas.

Properties of Nitric Oxide. — Nitric oxide is a colorless gas. In solid form it melts at $-150°$, and the liquid boils at $-142.4°$ under 757.2 mm. pressure. Its solubility in water is slight.

The density of the gas shows the formula to be NO; and there is no tendency to form a polymer, such as N_2O_2, even at low temperatures. This gas is the most stable of the oxides of nitrogen. Vigorously burning phosphorus continues to burn in the gas. Burning sulphur and an ignited taper, however, are extinguished.

Nitric oxide has two characteristic properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide:

$$2NO + O_2 \rightleftarrows 2NO_2.$$

The same result follows when it is led into warm concentrated nitric acid (*cf.* p. 293): $NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O$.

It also unites with a number of salts, the compound in the case of ferrous sulphate, $FeSO_4.NO$, being capable of existence in solution and possessing a brown color. Since ferrous sulphate will also reduce nitric acid to nitric oxide (p. 295), and the excess of the salt will then give a brown color with the product, a delicate test for nitric acid is founded upon these actions.

Preparation of Nitrogen Tetroxide NO_2. — This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

In most cases the oxide of the metal remains. When the mixed gases are led through a U-tube immersed in a freezing mixture, the tetroxide condenses as a pale-yellow liquid (b.-p. 22°), and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 295). It is likewise almost the sole product of the interaction of *concentrated* nitric acid and tin or copper (see p. 298). If the nitric oxide were produced by the primary action, it would be oxidized to nitrogen tetroxide in passing up through the acid (p. 295).

Properties of Nitrogen Tetroxide. — The most striking peculiarity of this gas is that, when hot, it is deep brown in color, but when cold, pale yellow. The density of the brown gas, at 14°, corresponds to the formula NO_2, that of the yellow gas at 22°, to N_2O_4. When the temperature is carried above 154°, by passing the brown gas through a red-hot tube, the brown color disappears, and nitric oxide and oxygen are formed. On cooling, the same steps through brown gas to pale-yellow gas are retraced:

$$\underset{\text{Colorless}}{2NO + O_2} \rightleftarrows \underset{\text{Brown}}{2NO_2} \rightleftarrows \underset{\text{Colorless}}{N_2O_4}.$$

Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, phosphorus burns readily in it: a taper, however, is extinguished. It has powerful oxidizing properties; and "fuming" nitric acid (p. 294), which contains it in solution, is employed when oxidation is the special object in view.

his oxide is intermediate in composition between nitrous and ic anhydrides, and, when dissolved in *cold* water, gives both ic and nitrous acids: $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$. If a base esent, a mixture of the nitrate and nitrite of the metal is produced. en the water is not cooled, the nitrous acid (*q.v.*), being unstable, s nitric oxide and nitric acid, so that the result is: $3NO_2 + H_2O$ $HNO_3 + NO$.

Oxidizing Actions of Nitric Acid.

'hen nitric acid gives up oxygen to any body, it is itself reduced. ce, according to convenience, we shall refer to oxidations by, or ictions of nitric acid.

xidation of Hydrogen. — The metals preceding hydrogen ie electromotive series (p. 245), displace hydrogen from nitric , as they do from other acids. With metals more active than , such as magnesium, a great part of the hydrogen escapes in the condition. But, in the case of zinc and the metals below it, t or all of the hydrogen is oxidized to water by the nitric acid, and of the acid is reduced (see Active hydrogen, p. 302). Thus, zinc and *very dilute* nitric acid, almost the only product, aside i zinc nitrate, is ammonia:

$$\begin{array}{rcll} 4Zn + & 8HNO_3 \rightarrow 4Zn(NO_3)_2\ (+\ 8H) & & (1) \\ (8H) + & HNO_3 \rightarrow NH_3 + 3H_2O & & (2) \\ NH_3 + & HNO_3 \rightarrow NH_4NO_3 & & (3) \\ \hline 4Zn + & 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O. & & \end{array}$$

i the excess of nitric acid (3), ammonium nitrate is formed.

eavy Metals. — The less active metals, such as copper and r, do not displace hydrogen from dilute acids (p. 245), but ce nitric acid, nevertheless, and are converted into nitrates. inum and gold (*cf.* p. 264) alone are not attacked. Thus, copper, somewhat *diluted* nitric acid, gives cupric nitrate and nitric e (NO).

making the equation for this action we may use a **plan** which is icable whenever an oxygen acid gives an oxide by reduction p. 260). We resolve the formula of nitric acid into those of

[illegible] is used with copp
[illegible]

$$2HNO_3 \rightarrow H_2O + 2NO_2 \ (+ O)$$
$$[illegible] + 2HNO_3 + Cu \rightarrow H_2O + Cu(NO_3)_2$$
$$4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO$$

[illegible] the constant production of [illegible] diluted nitric acid and the invariable formation of n[illegible] with concentrated acid. This is explained by the fac[illegible] [illegible] pass unchanged through a liquid c[illegible] [illegible] gives nitric acid and nitric oxide with the [illegible] where the nitric acid is concentrated, nit[illegible] if formed by the interaction with the metal, must [illegible] nitrogen tetroxide as it passes up through the liquid [illegible]

Oxidation of Non-Metals. — With non-metals [illegible] different in so far that these elements do not give n[illegible] sulphur boiled in nitric acid gives sulphuric acid, alo[illegible] oxide, equation [illegible], or with nitrogen tetroxide, equati[illegible] both, according to the concentration of the acid (see

$$2HNO_3 \rightarrow 2NO + H_2O \ (+ 3O)$$
$$(3O) + H_2O + S \rightarrow H_2SO_4$$
$$2HNO_3 + S \rightarrow 2NO + H_2SO_4$$

$$2HNO_3 \rightarrow 2NO_2 + H_2O + O \quad \times$$

although proceeding simultaneously in the same vessel (*cf.* p. 196). Thus the equation: $2HNO_3 + C \rightarrow H_2O + CO_2 + NO + NO_2$, is a misrepresentation. It implies that equimolar quantities of the two oxides of nitrogen are formed. But this could only occur by chance, and the balance would be destroyed the next moment by the lowering in the concentration of the acid, giving the advantage to the nitric oxide.

Oxidation of Compounds: Aqua Regia. — Compounds like hydrogen sulphide and sulphurous acid, which are easily oxidized, interact with nitric acid. With diluted nitric acid, the products are free sulphur and sulphuric acid respectively.

The mixture of nitric acid and hydrochloric acid is known as *aqua regia*. The chlorine set free by the oxidation of the hydrochloric acid is more active than is the ordinary solution of chlorine in water, perhaps in consequence of catalytic action of the substances in this solution (see Active hydrogen, p. 302), and combines with gold and platinum (*q.v.*), converting them into chlorides. Nitrosyl chloride (NOCl), which, however, does not interact directly with the noble metals, is formed also:

$$Cl\,H + H - O - \overset{\overset{\displaystyle O}{\|}}{N} = O + 2H\,Cl \rightarrow 2\,H_2O + Cl_2 + Cl - N = O$$

The interaction with platinum gives chloroplatinic acid:

$$2HCl + 2Cl_2 + Pt \rightarrow H_2PtCl_6.$$

Nitrous Acid, Hyponitrous Acid, and their Anhydrides.

Nitrites and Nitrous Acid. — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the **nitrites** remain:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2.$$

Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge (PbO) which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

When an acid is added to a dilute solution of a nitrite, a pale-blue solution containing **nitrous acid** HNO_2 is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

When a concentrated solution of sodium nitrite is acidified, the nitrous acid decomposes at once, and a brown gas containing the anhydride escapes:

$$2H^{\cdot} + 2NO_2' \leftrightarrows 2HNO_2 \leftrightarrows H_2O + N_2O_3 \uparrow.$$

This behavior distinguishes a nitrite from a nitrate.

Reducing agents deprive nitrous acid of part or all of its oxygen:

$$2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2.$$

Indigo is also converted by it into isatin (*cf.* p. 192). On the other hand, oxidizing agents which are sufficiently active, like acidified potassium permanganate, convert nitrous acid into nitric acid:

$$\begin{array}{rl} 3H_2SO_4 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O\ (+5O) & (1) \\ (5O) + 5HNO_2 \rightarrow 5HNO_3 & (2) \\ \hline 3H_2SO_4 + 2KMnO_4 + 5HNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3 & \end{array}$$

Nitrous acid is much used in the making of organic dyes.

Nitrous Anhydride N_2O_3. — A study of the gas arising from the decomposition of nitrous acid shows that in the gaseous state the anhydride is almost entirely dissociated:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

When the mixture is led through a U-tube immersed in a freezing mixture at $-21°$, a deep-blue liquid is obtained which is the anhydride itself. This dissociates when allowed to boil.

The same equimolar mixture of the two gases is obtained by the action of water on nitrosylsulphuric acid (p. 259).

Hyponitrous Acid and Nitrous Oxide N_2O. — Hyponitrous acid $H_2N_2O_2$ is a white solid. Its solution in water is an exceedingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:

$$H_2N_2O_2 \rightarrow H_2O + N_2O,$$

and this change is not capable of reversal.

Nitrous oxide is prepared by heating ammonium nitrate, or a mixture of a salt of ammonium and a nitrate:

$$NH_4NO_3 \rightarrow 2H_2O + N_2O.$$

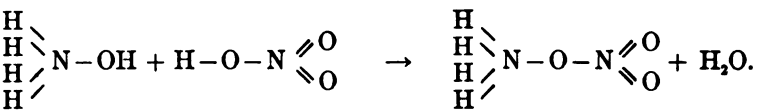
The steam condenses, and the nitrous oxide may be collected over warm water, or dried and compressed into steel cylinders.

Its solubility in cold water is considerable: at 0°, 130 volumes in 100; at 25°, 60 in 100. The liquefied gas boils at − 89.8° and its vapor tension at 20° is 49.4 atmospheres.

A glowing splinter of wood bursts into flame when introduced into nitrous oxide, and phosphorus, sulphur, and other combustibles burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free.

Metals do not rust in nitrous oxide, and the hæmoglobin of the blood is unable to use it as a source of oxygen. It is employed as an anæsthetic for minor operations. The symptoms which accompany its administration caused it to receive the name of " laughing gas."

Graphic Formulæ of Nitric Acid and its Derivatives: Explosives.—The following equation for the formation of ammonium nitrate by neutralization of ammonium hydroxide with nitric acid, shows the graphic (p. 156), or structural formulæ of these substances:



The structural formula of the nitrate is intended to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and attached to different nitrogen units. When the equilibrium of the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (p. 300) escapes with the steam.

The behavior of nitroglycerine and gun-cotton (p. 294), as well as of ammonium nitrite (p. 279), is explained in the same way. These substances are made by actions which, like the above neutralization, take place in the cold, and the groups, containing the oxygen on the one hand and carbon and hydrogen on the other, become quietly united without more serious interaction. When, however, the nitroglycerine, for example, is heated, or receives a mechanical shock, the carbon and hydrogen, all unite with the oxygen and the nitrogen escapes:

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2.$$

Active ("Nascent") Hydrogen. — When hydrogen gas is led through cold nitric acid, little or no action occurs. But (p. 297) when zinc, or some other metal which interacts with acids to give hydrogen, is placed in nitric acid the latter is reduced. To explain the apparent greater activity of the hydrogen in the second instance, we note the fact that it is liberated *on the surface of the zinc.* The contact effect (catalytic action) of the zinc increases its activity. Many metals have, in a greater or less degree, this power of increasing the activity of hydrogen. Thus, hydrogen absorbed in platinum or palladium (p. 73), or liberated by electrolysis on poles made of these metals, reduces nitric acid readily. Other elements, such as the chlorine in *aqua regia* (p. 299) and the oxygen in making sulphur trioxide (p. 257), are also rendered more active by contact agents.

This **more active** state of hydrogen is described as the **nascent state**, because it happens to be a common condition of hydrogen when associated with substances which produce it. The active state has, however, no necessary connection with such an immediately preceding act of liberation, as the platinum and sulphur trioxide illustrations, and the following experiment show: Three test-tubes are filled with very dilute potassium permanganate solution. Zinc dust, added to one, generates hydrogen and causes decolorization. A little platinum black is added to the second, and hydrogen gas is led through this and the third. The contact action of the platinum enables the hydrogen quickly to induce the permanganate, while the third portion remains unaltered.

Exercises. — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 295), and for all the actions concerned when the test for a nitrate (p. 296) is applied to sodium nitrate. What volume (at 0° and 760 mm.) of NO is obtained from one formula-weight of nitric acid (p. 144)?

2. Make correct equations for the formation of nitric oxide and nitrogen tetroxide by the action of carbon on nitric acid (p. 299).

3. Make equations for the interaction of iron with diluted and with concentrated nitric acid, respectively (p. 298). The iron gives ferric nitrate $Fe(NO_3)_3$.

4. Make a **classified list**, with examples, of all the kinds of interactions which, in this and preceding chapters, have been named **oxidations** and **reductions** (*e.g.* pp. 52, 53, 75, 110, 112, 192, 212, 253, 282, 297, 302. See also Chemistry of copper and tin).

CHAPTER XXVII

PHOSPHORUS

The Chemical Relations of the Element. — There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same valences, viz. three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen, NH_3 and PH_3, and both yield oxides of the forms X_2O_3, X_2O_4, and X_2O_5. The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids. The element is thus a non-metal.

Occurrence. — This element is found in nature in the form of phosphates. Calcium phosphate $Ca_3(PO_4)_2$, for example, occurs in most soils. It constitutes a large part of the solid material of the bones and teeth of animals and of the beds of fossil bones found in Florida and Tunis. A conspicuous mineral related to this substance is apatite, $Ca_5F(PO_4)_3$. It is found in large quantities in Canada, and is a component of many rocks. Complex organic compounds containing phosphorus are essential constituents of protoplasm and of the materials of the nerves and the brain.

Preparation. — Brand, merchant and alchemist, of Hamburg, discovered phosphorus (1669) by distilling the residue from evaporated urine, in the course of his search for the philosopher's stone. The mode of preparing it from **bone-ash**, which contains 83 per cent of calcium phosphate, was first published by Scheele (1771). Now the less expensive calcium phosphate of fossil origin is employed.

The powdered bone-ash or calcium phosphate and sulphuric acid (sp. gr. 1.5) are heated with steam and stirred in a wooden vat:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightleftarrows 2H_3PO_4 + 3CaSO_4\downarrow.$$

The calcium sulphate is precipitated during the heating, and subsequent concentration of the filtrate. This syrupy, crude phosphoric acid is mixed with carbon and then distilled in earthenware retorts. Two actions take place in succession. The phosphoric acid loses water and turns into metaphosphoric acid, then the latter is reduced by the carbon, carbon monoxide and phosphorus vapor passing off:

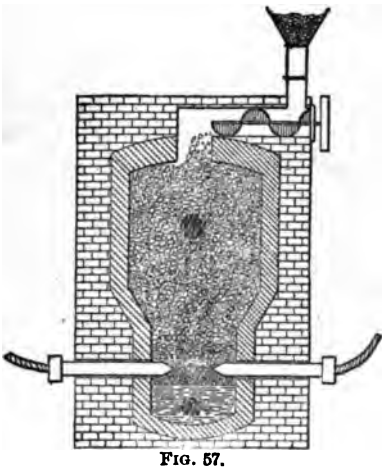


FIG. 57.

$$H_3PO_4 \rightarrow H_2O + HPO_3,$$
$$2HPO_3 + 6C \rightarrow H_2 + 6CO + 2P.$$

A pipe from the tubular clay retort conducts the vapors into cold water, in which the phosphorus collects.

A much simpler process depends on the use of the electric furnace (Fig. 57). The calcium phosphate is mixed with the proper proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into the furnace. The discharge of an alternating current between carbon poles produces the very high temperature which the action requires. The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals. The gaseous products pass off through a pipe and the phosphorus is caught under water:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P.$$

We may regard the phosphate as being composed of two oxides, $3CaO,P_2O_5$. It thus appears that the calcium oxide has united with the silica, which is an acid anhydride (*cf.* p. 258): $CaO + SiO_2 \rightarrow CaSiO_3$, while the phosphoric anhydride has been reduced.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

The Electric Furnace. — By an electric furnace is understood an **electro-thermal** arrangement in which the heat produced by some resistance offered to the current, such as that of an air-gap between

the carbons, is used to produce chemical change. Electrolysis plays no part in the phenomena, and an alternating current, which can produce no electrolytic decomposition, is generally employed. The restricted area within which the heat is developed makes possible the attainment of a high temperature (see Calcium carbide).

Physical Properties. — There are two perfectly distinct kinds of phosphorus, known as ordinary, or yellow phosphorus, and red phosphorus. **Yellow phosphorus**, prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. It melts at 44° and boils at 269°. Its molecular weight at 313° is 128 and the formula, therefore, P_4. Yellow phosphorus is soluble in carbon disulphide, less soluble in ether, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose. Continued exposure to its vapor causes necrosis, a disease from which match-makers are liable to suffer. The jawbones and teeth are particularly liable to attack.

Red phosphorus is a dull red powder consisting of small tabular crystals. It is obtained by heating yellow phosphorus to about 250° in a vessel from which air is excluded. A great amount of heat is evolved in the transformation.

Red phosphorus does not melt, but passes directly into vapor. Its vapor is identical with that of yellow phosphorus. It is insoluble in carbon bisulphide and other solvents. It is not poisonous, and, unlike yellow phosphorus, does not require to be kept under water to avoid spontaneous combustion.

Chemical Properties. — **Yellow phosphorus** unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together. The slow union of cold phosphorus with atmospheric oxygen is accompanied by the evolution of light, although the temperature is not such as we usually associate with incandescence. The name of the element (Gk. φῶς, light; φέρω, bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.* The

* The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of some animals, such as fireflies and some species of fish. In many violent chemical changes the light given out is con-

slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown (*cf.* p. 209).

Red phosphorus, since it is formed with evolution of heat, contains less energy than yellow phosphorus and is much less active. It does not catch fire in the air below 240°, while ordinary phosphorus ignites at 35–45°. When an element is known in two or more distinct forms, as is the case with oxygen, phosphorus, and carbon (*q.v.*), these substances are called **allotropic forms** of the element.

Matches. — In making common matches, which strike on any rough surface, the splints are first dipped in melted sulphur or paraffin to the extent of about half an inch. The head is often composed of manganese dioxide or red lead and a little potassium chlorate, which supply oxygen, a small proportion of free phosphorus (or sulphide of phosphorus) and antimony trisulphide, which are both combustible, and dextrin or glue.

In the case of "safety" matches, the mixture upon the head is not easily ignited by itself. It is composed of potassium chlorate or dichromate, some sulphur or antimony trisulphide, and a little powdered glass to increase the friction, all held together with glue. Upon the rubbing surface on the box is a thin layer of antimony trisulphide mixed with red phosphorus and glue. The friction converts a little of the red phosphorus into vapor.

Phosphine. — Three hydrides of phosphorus are known. These are, phosphine PH_3 (a gas), a liquid hydride P_2H_4, which is presumably the analogue of hydrazine (N_2H_4), and a solid hydride P_4H_2.

Phosphine PH_3 is formed slowly by the action of active hydrogen, from zinc and hydrochloric acid at 70°, upon yellow phosphorus. The gas may be made by boiling yellow phosphorus with potassium hydroxide solution. Potassium hypophosphite is formed at the same time:

$$3KOH + 4P + 3H_2O \rightarrow 3KH_2PO_2 + PH_3.$$

The gas made in this way contains a little of the vapor of the liquid

spicuously greater than that proper to the temperature produced (*cf.* p. 53), and must come, therefore, in part, directly from the chemical energy. Thus, burning magnesium has a temperature of about 1350°, while the production of light of the same character, by mere incandescence, would require a temperature of about 5000°.

hydride, which is spontaneously inflammable, and consequently the mixture catches fire on emerging from the delivery tube.

The simplest method of preparing phosphine is by the action of water upon calcium phosphide:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

This action is analogous to that of water upon magnesium nitride (p. 281), by which ammonia is produced. In consequence of the fact that calcium phosphide is a substance of irregular composition, a mixture of all three hydrides is generally obtained. By passing the gas through a strongly cooled delivery tube, however, the liquid compound is condensed and fairly pure phosphine passes on.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. When burned it forms phosphoric acid. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and produces no basic compound corresponding to ammonium hydroxide when brought in contact with this substance. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it does not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4.$$

Phosphonium Compounds. — Hydrogen iodide unites with phosphine to form a colorless solid crystallizing in beautiful, highly refracting, square prisms: $PH_3 + HI \rightarrow PH_4I$. Hydrogen chloride combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at 14°. When the pressure is released, rapid dissociation occurs.

In imitation of the ammonia nomenclature, these substances are called phosphonium iodide and phosphonium chloride PH_4Cl. They are entirely different, however, from the corresponding ammonium derivatives, for the $PH_4^{\cdot}$ ion is unstable. When brought in contact with water they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

Halides of Phosphorus. — The existence of the following halides has been proved conclusively:

. . . .	. . . . .	. . . . .	P_2I_4 (solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	. . . . .

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all hydrolyzed by water, and give an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 162) and hydrogen iodide (p. 167).

Phosphorus trichloride PCl_3 is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. The substance, which is a liquid boiling at 76°, is stable (*cf.* p. 284). When excess of chlorine is employed, **phosphorus pentachloride** PCl_5, which is a white solid body, is formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In the case of the interaction of phosphorus pentachloride and water, phosphoric acid is formed:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl.$$

Phosphorus pentachloride, when heated, reaches a vapor tension of 760 mm. at 140°, and while still solid. It therefore passes freely into vapor (boils, so to speak) at this temperature, and condenses directly to the *solid* form. This sort of distillation is called **sublimation.** At a pressure above that of the atmosphere it melts at 148°. Partial dissociation occurs in the vapor (*cf.* pp. 146, 181).

Oxides of Phosphorus. — The oxides of phosphorus are the so-called trioxide P_4O_6, the pentoxide P_2O_5, and a tetroxide P_2O_4.

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form metaphosphoric acid (see below), and hence is known as **phosphoric anhydride**: $P_2O_5 + H_2O \rightarrow 2HPO_3$. In the laboratory this action is frequently utilized for drying gases (p. 287) and for removing water from combination (p. 294).

The **trioxide** P_4O_6 is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at 22.5° and boiling at 173°. This oxide is the anhydride of phosphorous acid, but it unites exceedingly slowly with cold water to form this substance. It interacts vigorously with hot water, but phosphine, red phosphorus, hypophosphoric acid, and phosphoric acid are amongst the products, and very little phosphorous acid escapes decomposition. When this oxide is heated to 440° it decomposes, giving the **tetroxide** P_2O_4 and red phosphorus.

Acids of Phosphorus. — There are six different acids of phosphorus. Three are phosphoric acids, representing the same stage of oxidation of phosphorus, but different degrees of hydration of the anhydride. The others show three different and lower states of oxidation:

Orthophosphoric acid	H_3PO_4 ($= 3H_2O,P_2O_5$)
Pyrophosphoric acid	$H_4P_2O_7$($= 2H_2O,P_2O_5$)
Metaphosphoric acid	HPO_3 ($= H_2O,P_2O_5$)
Hypophosphoric acid	$H_4P_2O_6$($= 2H_2O,P_2O_4$)
Phosphorous acid	H_3PO_3 ($= 3H_2O,P_2O_3$)
Hypophosphorous acid	H_3PO_2 ($= 3H_2O,P_2O$)

The Phosphoric Acids. — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide (the anhydride) and water. In the majority of cases already considered this sort of action takes place in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water: $N_2O_5 + H_2O \rightarrow 2HNO_3$. Similarly, the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water: $SO_3 + H_2O \rightarrow H_2SO_4$, although here we have also disulphuric acid $H_2S_2O_7$, or $H_2O,2SO_3$.

Now, when phosphoric anhydride acts upon water we obtain a solution which, on immediate evaporation, leaves a glassy solid, HPO_3, known as metaphosphoric acid. This is H_2O, P_2O_5. When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid, whose hydrogen-ion acts catalytically, the residue from evaporation is H_3PO_4, orthophosphoric acid:

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \text{ or } HPO_3 + H_2O \rightarrow H_3PO_4.$$

This acid is $3H_2O$, P_2O_5, and no further addition of water can be effected.

Conversely, when orthophosphoric acid is kept at about 255° for a time, it slowly loses water, and $H_4P_2O_7$, pyrophosphoric acid, is obtained:

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$

This acid is $2H_2O$, P_2O_5. Further desiccation leaves metaphosphoric acid, which cannot be further resolved into phosphorus pentoxide and water. When dissolved in water, pyrophosphoric

acid slowly resumes the water which it has lost and gives the ortho-acid again. The pyro-acid does not seem to be formed by hydration of the meta-acid, but only by dehydration of the ortho-acid. The relations of all these substances are more clearly seen in the graphic formulæ:

$$\begin{array}{l} P\left\{\begin{array}{l} =O \\ -O-H \\ -O-H \\ -O-H \end{array}\right. \\ \\ P\left\{\begin{array}{l} -O-H \\ -O-H \\ -O-H \\ =O \end{array}\right. \end{array} \rightarrow \begin{array}{l} P\left\{\begin{array}{l} =O \\ -O-H \\ -O-H \\ O \end{array}\right. \\ P\left\{\begin{array}{l} -O-H \\ -O-H \\ =O \end{array}\right. \end{array} \rightarrow \begin{array}{l} P\left\{\begin{array}{l} =O \\ -O-H \\ =O \end{array}\right. \\ P\left\{\begin{array}{l} =O \\ -O-H \\ =O \end{array}\right. \end{array} \leftarrow \begin{array}{l} P\left\{\begin{array}{l} =O \\ =O \\ O \end{array}\right. \\ P\left\{\begin{array}{l} =O \\ =O \end{array}\right. \end{array}$$

A most important fact to be noted is that the *addition or removal of water leaves the valence of the phosphorus unchanged.* The degree of oxidation of the phosphorus and its valence are *identical* in the three acids.

The Relations of Anhydrides and Oxygen Acids. — Considering the anhydride from which an acid is derived gives us the key to the nature and behavior of the acid. It tells much that the formula of the acid does not tell. For example: (1) What is the valence of phosphorus in H_3PO_3? The only way to answer this question is to resolve the formula (doubled, if necessary) into water and the anhydride, $3H_2O,P_2O_3$. The phosphorus is trivalent. (2) How is this acid related to metaphosphoric acid HPO_3? Resolve the latter, as before, H_2O,P_2O_5. The answer is that in the latter the phosphorus is quinquivalent. (3) How can we get phosphorous acid from metaphosphoric acid, or *vice versa?* Considering the anhydrides, we answer, by reduction and oxidation, respectively. (4) Is pyrophosphoric acid $H_4P_2O_7$, because it contains 7O, to be made from all others by oxidation? Resolve it into water and anhydride, $2H_2O,P_2O_5$. We then perceive that to make it from phosphorous acid requires oxidation, but to make it from ortho- or metaphosphoric acid requires only a change in the degree of hydration: *adding or subtracting water*, since it adds or subtracts hydrogen and oxygen in equivalent amounts, *is not oxidation or reduction.* These conceptions have been used before (*e.g.* pp. 260, 297, 309).

Considerations like the foregoing are never for a moment absent from the mind of a chemist when he is thinking about oxygen acids. Every such acid is to him always a certain anhydride, plus a certain proportion of water (see Exercises 1 and 2). He applies the same method to salts, subtracting the oxide of the metal ($CaSO_4 = CaO,SO_3$) to determine the valence and state of oxidation of the non-metallic element in the compound.

Orthophosphoric Acid H_3PO_4 and Its Salts.— As we have seen (p. 303), ordinary calcium phosphate is the **source** of the impure, commercial acid. Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating the water and excess of nitric acid. The product is a white, crystalline, deliquescent solid.

This acid is **much weaker** than sulphuric acid, and is dissociated chiefly into the ions $H^{\cdot}$ and H_2PO_4'. The dihydrophosphate-ion is broken up to some extent into $H^{\cdot}$ and HPO_4'', as we learn from the fact that the solution of the sodium salt NaH_2PO_4 is acid. The ion HPO_4'' is hardly dissociated at all, for a solution of the salt Na_2HPO_4 is not acid in reaction.

As a **tribasic acid**, it forms salts of three kinds, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. These are known respectively as **primary**, **secondary**, and **tertiary** sodium orthophosphate. The primary sodium phosphate is faintly acid in reaction. The secondary one is slightly alkaline, because of hydrolysis arising from the tendency of the hydrogen-ion of the water to combine with the HPO_4'' to form H_2PO_4', which is much more feebly acid than is phosphoric acid H_3PO_4. The simplified equation (p. 254) shows the reason for the alkalinity of the solution: $HPO_4'' + H^{\cdot} + OH' \rightarrow H_2PO_4' + OH'$. The tertiary phosphate is stable only in solid form, and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O \uparrow.$$

When the product is dissolved in water, the action is reversed (*cf.* p. 253). Mixed phosphates are also known, particularly sodium-ammonium phosphate (**microcosmic salt**) $NaNH_4HPO_4$, $4H_2O$, and the insoluble magnesium-ammonium phosphate $MgNH_4PO_4$. Primary calcium phosphate (*q.v.*), known in commerce as "superphosphate," is used as a fertilizer.

The tertiary **phosphates** are unchanged by **heating**. The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O,$$
$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O.$$

It will be seen that the **meta-** and **pyrophosphates of sodium** are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (*cf.* p. 283). Thus, microcosmic salt gives primary sodium phosphate:

$$NaNH_4HPO_4 \rightarrow NH_3 + NaH_2PO_4 \rightarrow NaPO_3 + H_2O,$$

and this in turn is converted into the metaphosphate by loss of water.

Pyrophosphoric Acid and Metaphosphoric Acid. — **Pyrophosphoric acid** $H_4P_2O_7$, although tetrabasic, gives only the neutral salts, such as $Na_4P_2O_7$, and those in which one-half of the hydrogen has been displaced by a metal, such as $Na_2H_2P_2O_7$.

Metaphosphoric acid HPO_3 is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula $(HPO_3)_2$.

Sodium metaphosphate $NaPO_3$, in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead**, and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate: $NaPO_3 + H_2O \rightarrow NaH_2PO_4$. In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed orthophosphates. Thus, with

oxide of cobalt a part of the metaphosphate unites according to the equation:

$$NaPO_3 + CoO \rightarrow NaCoPO_4,$$

and the product confers a blue color on the bead.

Distinguishing Tests. — When a solution of nitrate of silver is added to a solution of orthophosphoric acid or any soluble orthophosphate, a yellow precipitate of silver orthophosphate Ag_3PO_4 is produced. This is a test for phosphate-ion. With pyrophosphoric acid or any pyrophosphate the product is white $Ag_4P_2O_7$. With metaphosphoric acid a white precipitate, $AgPO_3$, is obtained also. Metaphosphoric acid coagulates a clear solution of albumen, while pyrophosphoric acid has no visible effect upon it.

Phosphorous Acid H_3PO_3. — When added to cold water phosphorus trioxide (P_4O_6) yields phosphorous acid very slowly. With hot water the action is exceedingly violent and complex (p. 308). This acid may be obtained also by the action of water upon phosphorus trichloride, tribromide (p. 162), or tri-iodide and evaporation of the solution:

$$PCl_3 + 3H_2O \rightarrow P(OH)_3 + 3HCl.$$

A certain amount of this acid, along with phosphoric acid and hypophosphoric acid, is formed when moist phosphorus oxidizes in the air.

In spite of the presence of three hydrogen atoms, this acid is dibasic, and two only are replaceable by metals. To express this fact, the first of the following formulæ is preferred:

$$O = P\begin{cases} -\,H \\ -\,O\,-\,H \\ -\,O\,-\,H \end{cases} \qquad P\begin{cases} -\,O\,-\,H \\ -\,O\,-\,H \\ -\,O\,-\,H \end{cases}$$

since the symmetrical formula would indicate no difference between the three hydrogen atoms. H united directly to P, as here and in PH_3, is not acidic. Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (*cf.* pp. 191, 196, 199, 266, 299), namely, metaphosphoric acid, and phosphine:

$$4H_3PO_3 \rightarrow 3HPO_3 + 3H_2O + PH_3.$$

Sulphides of Phosphorus. — Yellow phosphorus when heated with sulphur unites with explosive violence. By using red phosphorus the action can be controlled. By employing the proper proportions the **pentasulphide** P_2S_5 is secured. It is purified by distillation, and is a yellow crystalline mass (m.-p. 274°, b.-p. 530°). Phosphorus pentasulphide is hydrolyzed by cold water:

$$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S.$$

Other sulphides, P_4S_3, P_2S_3, and P_3S_6, may be prepared by using the constituents in the proportions represented by these formulæ.

Comparison of Phosphorus with Nitrogen and with Sulphur. — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The differences are seen in the facts that nitrogen is a gas and exists in but one form, while phosphorus is a solid occurring in two varieties, and that the former is inactive and the latter active. The contrasts between phosphine and ammonia (p. 307) and between the halides of the two elements (pp. 284, 308) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the facts, that hydrogen sulphide does not unite with the hydrogen halides at all while phosphine gives the phosphonium halides, and that phosphoric acid is hard to reduce while sulphuric acid is reduced with comparative ease.

Exercises. — 1. What are the valences of the non-metals in: $H_2S_2O_7$, $H_2Cr_2O_7$, $KMnO_4$, KH_2PO_2, H_3NO_4, NaH_2PO_3, $Na_2P_2O_6$. Name these substances.

2. Is it oxidation or reduction, or neither, when we make, (*a*) N_2O_4 from HNO_3, (*b*) SO_2 from H_2SO_3, (*c*) HPO_3 from H_3PO_3, (*d*) $H_2S_2O_7$ from H_2SO_4, (*e*) Na_2SO_4 from $NaHSO_3$?

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 253) be less suitable than nitric acid, as an oxidizing agent for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 311) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolyses of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (p. 253).

6. How should you prepare $Ca_2P_2O_7$ and $Ca(PO_3)_2$?

7. What product should you confidently expect to find after heating (p. 313), (*a*) sodium phosphite, Na_2HPO_3, (*b*) potassium hypophosphite? Make the equations.

8. Compare the elements chlorine and phosphorus after the manner of the comparisons on p. 314.

CHAPTER XXVIII

CARBON AND THE OXIDES OF CARBON

The Chemical Relations of the Element. — The elements of the carbon family (p. 276) are carbon, silicon, germanium, tin, and lead. Of these the first two are entirely non-metallic, while the others are metallic elements showing more or less strong resemblances to the non-metals. All these elements are quadrivalent. With the exception of silicon, however, they all form compounds in which they are bivalent.

On account of the fact that the majority of the substances composing, and produced by, living organisms are compounds of carbon, the chemistry of these compounds is known as organic chemistry. It was at first supposed that the artificial production of such compounds, *e.g.* without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, a process called **synthesis**, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, hundreds of compounds unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of chemical compounds.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these, nitrogen, phosphorus, the halogens, and sulphur may be named.

Carbon C.

Occurrence. — Large quantities of carbon are found in the free condition in nature. The diamond is the purest natural carbon. Graphite, or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. Coal occurs in numerous forms containing greatly varying proportions of free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in marsh-gas, or methane CH_4,

which is the chief component of natural gas. The mineral oils consist almost entirely of mixtures of various compounds of carbon and hydrogen. Whole geological formations are composed of carbonates of common metals, particularly calcium carbonate or limestone, and a double carbonate of calcium and magnesium, known as dolomite.

The Diamond. — The allotropic forms (p. 306) of carbon differ very markedly in their physical properties. Diamonds, which are found in India, Borneo, Brazil, and South Africa, are scattered sparsely through metamorphic and volcanic rocks which seem to have undergone secondary changes. They are covered with a crust which entirely obscures their luster, and possess natural crystalline forms belonging to the regular system. A form related to the octahedron (p. 94) is frequently observed. It should be noted that this natural form bears no relation whatever to the pseudo-crystalline shape which is conferred upon the stone by the diamond-cutter. Thus, a "brilliant" possesses one rather large, flat face, which forms the base of a many sided pyramid (Fig. 58, showing two views). This form is given to the stone, in order that the maximum reflection of light from its interior may be produced. The diamond is harder than any other variety of matter, with the exception, perhaps, of one compound of boron, while only one or two other materials, like carborundum, approach it. Its specific gravity is about 3.5, and it is the densest form of carbon. Few materials are capable of dissolving any of the forms of carbon. Molten iron (*q.v.*) dissolves five or six per cent, part of which goes into combination; but usually only graphite is found in the cooled product. Moissan (1887), however, succeeded in preparing microscopic fragments of diamonds in this way. The diamond is a nonconductor of electricity.

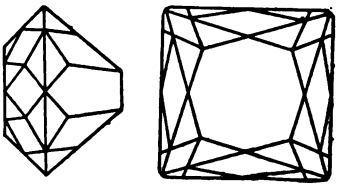


FIG. 58.

The largest diamond known, the *Cullinan*, weighs 621 g. (uncut). The *Kohinoor* weighs 22 g.

That the diamond contains nothing but carbon, is shown by the fact that when burned it produces nothing but carbon dioxide.

Graphite.—Graphite (Gk. γράφω, I write) is found in Cumberland, Siberia, and Ceylon. The form appears to belong to the hexagonal system. The mineral is extremely soft, in utter contrast to the diamond, and has a smaller specific gravity (about 2.3). It conducts electricity. It is made artificially by an electro-thermal process (*cf.* p. 304). A powerful alternating current is passed through a mass of granular anthracite, and the latter, although not melted by the high temperature, is largely converted into graphite.

Graphite is now used exclusively for making the anodes in the electrolytic manufacture of chlorine and in related processes. Mixed with fine clay it forms the "lead" of lead pencils. As "black-lead", it is employed to protect ironware from rusting. It is used as a lubricant in cases where oil would be decomposed by heat.

Amorphous Carbon.—This is the name given to the varieties of the element which have no crystalline form. They vary in specific gravity up to 1.9. **Coke**, which is now manufactured in immense quantities by heating coal until all the volatile matter has been distilled off, is a very dense variety of amorphous carbon. It is used in the reduction of iron ores.

By the imperfect combustion of heavy oils and resins, in which the flame plays upon a cooled surface, a finely divided form of carbon, **lampblack**, is produced. This is used in making printer's ink.

Charcoal is chiefly made by the heating of wood out of contact with air. In the more refined forms of the process the charring is conducted in retorts, and the materials which distil off are used in various ways. Wood consists largely of cellulose $(C_6H_{10}O_5)_n$, incrusted with lignin and holding much moisture and resinous material. The products of its distillation are partly gaseous and partly fluid. The gases, consisting mainly of hydrogen, methane CH_4, ethane C_2H_6, ethylene C_2H_4, and carbon monoxide CO, are employed, on account of their combustibility, as fuel in the distillation itself. The fluids form a complex mixture containing large quantities of water, methyl alcohol CH_3OH (wood spirit), acetic acid, acetone $(CH_3)_2CO$, and tar. Wood charcoal exhibits the cellular structure of the material from which it was made, and is therefore highly porous. When the charcoal is burned, the mineral constituents of the wood appear in the ash.

For certain purposes, charcoals made, in the same fashion as the

above, from bones and from blood, find wide application. The former, called **bone black**, contains much calcium phosphate (p. 303). In the chemical laboratory, **pure carbon** is made, as a rule, by the charring of sugar (cane-sugar, $C_{12}H_{22}O_{11}$).

The tendency of almost all carbon compounds to char, when heated, is used as a means of recognizing their presence.

Properties of Charcoal. — Charcoal exhibits certain properties which are not shared to any extent by other forms of carbon. For example, it can take up large quantities of many gases. Boxwood charcoal will in this way absorb ninety times its own volume of ammonia, fifty-five volumes of hydrogen sulphide, or nine volumes of oxygen. Freshly made dogwood charcoal (used in making the best gunpowder), when pulverized immediately after its preparation, often catches fire spontaneously on account of the heat liberated by the condensation of oxygen. It is therefore set aside for two weeks, to permit the slow absorption of moisture and air, before being ground up. The absorbed gases may be removed unchanged by heating the charcoal in a vacuum. The disappearance of these immense quantities of gas into small pieces of charcoal is described as **adsorption**, and is caused by the *ad*hesion of the gases to the very extensive internal surface which the charcoal possesses. Glass shows the same property, though in a smaller degree (p. 80). Solid and liquid bodies are also in many cases taken up by charcoal in a similar fashion. Thus, strychnine may be removed from an aqueous solution by agitation of the latter with charcoal. In the manufacture of whiskey (*q.v.*), the fusel oil, which is extremely harmful, is in many cases removed by filtration of the diluted spirit through charcoal, before rectification. Organic coloring matters, such as litmus and indigo, belong to the class of bodies thus extracted from solution by charcoal. In the refining of sugar the syrup is boiled with charcoal for the purpose of removing a brown resin, in order that the product may be perfectly white. It is, in part, upon this property that we rely, also, in the employment of charcoal filters. The organic materials dissolved in the drinking water undergo adsorption in the charcoal. In this connection, however, it must be remembered that the quantity which a given mass of charcoal may take up is limited, and that careful cleansing is required in order that the efficiency of the filter may be maintained.

Coal. — Peat, brown coal, soft coal, and anthracite represent, in a general way, different stages in the decomposition of vegetable matter in absence of air. Water and compounds of carbon and hydrogen are given off in the process. The following table shows this change in composition and the relations of the substances to fresh wood on the one hand and charcoal and coke on the other:

	Percentage, excluding Ash and Moisture, of:				Percentage Ash.	Percentage of Water (Air Dried).	Calorific Value per g. in Calories.
	C	H	O	N			
Wood	45	6	48	1	1.5	18–20	2700
Peat	60	6	32	2	5–20	20–30	3500
Brown coal . .	70	5	24	1	3–30	15	30–6000
Soft coal	82	5	12	1	1–15	4	66–8000
Anthracite . . .	94	3	3	...	1.5	2	70–8000
Charcoal	95	1.7	3.4	...	4	6.5	8000
Coke	96	0.7	2.5	1	3.4–11	2	7700

Chemical Properties of Carbon. — The most common uses of carbon depend upon its great tendency to unite with oxygen, forming carbon dioxide. Under some circumstances carbon monoxide is produced. Aside from the direct employment of this action for the sake of the heat which is liberated, it is used also in the reduction of ores of iron, copper, zinc, and many other metals. When, for example, finely powdered cupric oxide and carbon are heated, copper is obtained. The gas given off is either carbon dioxide, or a mixture of this with carbon monoxide, according to the proportion of carbon used:

$$CuO + C \rightarrow Cu + CO,$$
$$2CuO + C \rightarrow 2Cu + CO_2.$$

Carbon unites directly with hydrogen very reluctantly. When an electric arc is produced between carbon poles in a tube through which hydrogen passes, traces of acetylene C_2H_2 are formed.

At the high temperatures produced in the electric furnace, carbon unites with many metals and some non-metals. Compounds formed in this way are known as carbides, such as aluminium carbide Al_4C_3, calcium carbide CaC_2, and carborundum CSi.

Calcium Carbide CaC_2. — This compound, which is colorless when pure, is manufactured in an electric furnace, by the interaction of finely pulverized limestone or quicklime with coke:

$$CaO + 3C \rightarrow CaC_2 + CO.$$

The operation is a continuous one, the materials being thrown into the left side of the drum (Fig. 59, diagrammatic), and the product removed on the right. The carbon poles are fixed. The arc having been established, the drum is rotated slowly as the carbide accumulates. The current enters by one carbon, passes through the carbide, and leaves by the other. The high resistance of the partially transformed material causes the production of the heat. When the action in one layer approaches completion, the resistance falls, the current increases, and an armature round which the wire passes (not shown in Fig. 59) comes into operation and turns the drum. In this way the carbide just formed is continuously moved away from the carbons, and new material, introduced on the left, falls into the path of the current. The iron plates which form the circumference of the drum are added on the left and removed on the right, where also the carbide is broken out with a chisel. The drum revolves once in about three days. The product is used for making acetylene (*q.v.*).

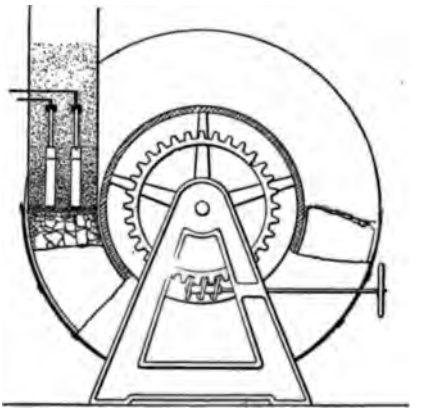


FIG. 59.

CARBON DIOXIDE AND CARBONIC ACID.

Occurrence. — Carbon dioxide is present in the atmosphere, and issues from the ground in large quantities in certain neighborhoods, as, for example, near the Lake of Laach, in the so-called Valley of Death in Java, and in the Grotta del Cane near Naples. Effervescent mineral waters contain it in solution, and their effervescence is

caused by the escape of the gas when the pressure is reduced. Well-known waters of this kind are those of Selters and of the Geyser Spring at Saratoga.

Modes of Formation. — Carbon dioxide is produced by combustion of carbon in the presence of an excess of oxygen:

$$C + O_2 \rightarrow CO_2.$$

The combustion of all compounds of carbon, as well as the slow oxidation in the tissues of plants and animals, yield the same product.

It was Joseph Black (1757) who first recognized the gas as a distinct substance. He observed its formation when marble or magnesium carbonate was heated:

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

and named the gas "fixed air" from the fact that it was contained in these solids. The above action had been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting the normal carbonates of potassium and sodium, decompose in this way, leaving the oxide of the metal.

Black found that the gas was also produced when acids acted upon carbonates, and this method is commonly employed in the laboratory:

$$CaCO_3\,(\text{solid}) \leftrightarrows \left.\begin{array}{l} CaCO_3\,(\text{dslvd}) \leftrightarrows Ca^{\cdot\cdot} + CO_3'' \\ 2HCl\,(\text{dslvd}) \leftrightarrows 2Cl' + 2H^{\cdot} \end{array}\right\} \leftrightarrows H_2CO_3 \leftrightarrows H_2O + CO_2.$$

Since the carbonic acid is very slightly ionized, the action is like that of acids on sulphites (p. 256). The carbonate of calcium, however, is very slightly soluble, so that an additional equilibrium controls its solution. In this respect the action is like that of acids on ferrous sulphide (p. 251).

Carbon dioxide is formed in decay (p. 287) and in fermentation (*q.v.*).

Physical Properties. — Carbon dioxide is a colorless, odorless gas. It is heavier than air. The G.M.V. weighs 44.26 g. Liquefied carbon dioxide boils at — 79°. The sp. gr. of the liquid at 0° is 0.95. At 0° its vapor tension is 35.4 atmospheres and at 20° 59 atmospheres. It must be preserved, therefore, in very strong cylinders of mild steel. Large quantities of it, often collected from fermentation vats, are sold in such cylinders, and used in operating beer-pumps and in making aerated waters. When the liquid is allowed

to flow out into an open vessel it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates without melting (*cf.* p. 308).

Carbon dioxide gas (760 mm. and 15°) dissolves in its own volume of water. Up to four or five atmospheres Henry's law describes its solubility accurately. An aqueous solution, under a pressure of 2–3 atmospheres, is familiarly known as *soda-water*.

Chemical Properties. — Carbon dioxide is a stable compound. At 2000°, the dissociation reaches 7.5 per cent, or about four times that of water: $2CO_2 \rightleftarrows 2CO + O_2$.

The more active metals, like magnesium, burn brilliantly when ignited in a cupel-shaped lump of solid carbon dioxide, producing the oxide and free carbon. Less active metals, such as zinc and iron, give an oxide and carbon monoxide (*q.v.*).

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium, sodium, calcium, etc. Hence the decomposition of calcium carbonate by heating (p. 322) is a reversible action.

Carbon dioxide, when dissolved in water, forms an unstable acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3.$$

The name carbonic acid is frequently, though improperly, given to the anhydride CO_2, which has no acid properties.

Chemical Properties of Carbonic Acid H_2CO_3. — The solution of carbon dioxide in water exhibits the properties of a weak acid. It conducts electricity, although not well. It turns litmus red. The ionization takes place chiefly according to the equation:

$$H_2CO_3 \rightleftarrows H^{\cdot} + HCO_3'.$$

Carbonates and Bicarbonates — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed into a solution of the alkali, water is formed and the acid carbonate (bicarbonate) remains dissolved:

$$H_2CO_3 + NaOH \leftrightarrows H_2O + NaHCO_3, \text{ or } H^{\cdot} + OH' \rightarrow H_2O.$$

Although the bicarbonate is technically an acid salt, its solution is neutral on account of the exceedingly slight dissociation of the HCO_3'

ion. By addition of an equivalent of sodium hydroxide the normal carbonate is obtained:

$$NaOH + NaHCO_3 \rightleftarrows H_2O + Na_2CO_3, \quad \text{or} \quad OH' + HCO_3' \rightleftarrows H_2O + CO_3''.$$

This solution, like that of all salts of a strong base and a feeble acid (*cf.* p. 254), is alkaline in reaction. This is because the tendency to form the very slightly ionized HCO_3' makes the foregoing ionic action noticeably reversible (*cf.* pp. 254, 311).

The normal carbonates, with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example:

$$BaCl_2 + Na_2CO_3 \rightleftarrows BaCO_3\downarrow + 2NaCl \quad \text{or} \quad Ba^{\cdot\cdot} + CO_3'' \rightleftarrows BaCO_3\downarrow.$$

The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner:

$$Ca(OH)_2 + H_2CO_3 \leftrightarrows CaCO_3\downarrow + H_2O.$$

These precipitations are used as tests for carbon dioxide.

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" are frequently held in solution by natural waters:

$$H_2CO_3 + CaCO_3 \rightleftarrows H_2Ca(CO_3)_2.$$

In the same fashion, the carbonates of iron ($FeCO_3$), magnesium, and zinc are somewhat soluble in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action. Water containing "lime" in solution is known as *hard water* (*q.v.*).

Rôle of Chlorophyll-bearing Plants in Storing Energy.— While in plants the same consumption of oxygen and production of carbon dioxide goes on as in animals, only with less rapidity, an action which is in a general way a reversal of this takes place at the same time. The chlorophyll and protoplasm in the leaves of the plant have the power of taking up carbon dioxide. Part of the oxygen is restored to the air, and the rest of the substance, including all the carbon, is used by the plant as food. This operation goes on only in sunlight. The various chemical compounds which plants construct in large quantities, of which sugar, starch, and cellulose

are prominent examples, are built up as the result of this action. We may represent the production of cellulose by means of the equation:

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 - 671{,}000 \text{ calories.}$$

The energy absorbed in this action is furnished by the sunlight. The same amount is recovered when the wood is burned, and the action reversed.

Carbon Monoxide CO.

Preparation.— Carbon monoxide is formed in many industrial operations. We commonly observe the blue flame of burning carbon monoxide playing on the surface of a coal fire. The gas is produced by the passage of the carbon dioxide, which is first formed, through the upper layers of heated coal:

$$CO_2 + C \rightarrow 2CO.$$

A similar reduction of carbon dioxide is produced by metals such as zinc, when a moderate heat is applied:

$$CO_2 + Zn \rightarrow ZnO + CO.$$

On a large scale, a mixture of carbon monoxide and hydrogen is known as **water gas**. Steam is turned into an iron cylinder lined with fire clay and filled with vigorously burning coke:

$$C + H_2O \rightarrow CO + H_2.$$

The products are both combustible, and, by the addition of substances which burn with a luminous flame, the mixture is used for the manufacture of illuminating-gas (*q.v.*).

In the laboratory, carbon monoxide is frequently obtained by heating oxalic acid, a solid, white, crystalline substance, with concentrated sulphuric acid. The latter is here employed simply as a dehydrating agent (p. 263), so that it need not be included in the equation:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

To obtain pure carbon monoxide from this mixture it is necessary to remove the carbon dioxide by passing the gas through a solution of potassium hydroxide. By using formic acid, or sodium formate, with sulphuric acid, the presence of the carbon dioxide is avoided:

$$HCHO_2 \rightarrow CO + H_2O.$$

Physical Properties.—Carbon monoxide is a colorless, tasteless, odorless gas. It is very slightly soluble in water. Its density is almost the same as that of air. When liquefied it boils at − 190°.

Chemical Properties. — All the chemical properties of carbon monoxide are referable to the fact that in it the element carbon appears to be bivalent: C=O. The compound is in fact unsaturated, and combines with oxygen, chlorine, and other substances directly. Thus the gas burns in the air, uniting with oxygen to form carbon dioxide. Again, iron (*q.v.*) is manufactured by the reduction of the oxide of iron by gaseous carbon monoxide in the blast furnace:

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2.$$

In sunlight carbon monoxide unites directly with chlorine to form **carbonyl chloride** $COCl_2$. It unites directly with nickel and iron to form nickel carbonyl and iron carbonyl (*q.v.*), respectively.

The gas is an active poison. When inhaled it unites with the hæmoglobin of the blood to the exclusion of the oxygen which forms a less stable compound (*cf.* p. 52). A quantity equivalent to about 10 c.c. of the gas per kilo. weight of the animal is sufficient to produce death, about one-third of the whole hæmoglobin having entered permanently into combination with carbon monoxide.

Carbon Disulphide CS_2.—This compound is made by direct union of sulphur vapor and glowing charcoal. An electric furnace like that in Fig. 57 (p. 304) is employed. The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid (b.-p. 46°). Traces of other compounds give the commercial article a disagreeable smell. It burns in air, forming carbon dioxide and sulphur dioxide. Iodine, phosphorus, sulphur, and rubber dissolve freely in it.

Exercises. — 1. To which of the factors in the interaction of calcium carbonate and hydrochloric acid (p. 322) is due the forward displacement of all the equilibria?

2. What will be the excess of pressure inside a bottle of soda-water when four volumes of carbon dioxide are dissolved in one volume of water?

3. What volume of liquid carbon dioxide, measured at 0°, will be required to give 75 liters of the gas at 0° and 760 mm. pressure?

4. What are the exact relative weights of equal volumes of carbon dioxide, carbon monoxide, air, and steam?

CHAPTER XXIX

SOME CARBON COMPOUNDS

THE compounds of carbon with hydrogen are called **hydrocarbons.** Those containing oxygen, as well, are divided into numerous and extensive groups according to their behavior. Thus there are **acids** like acetic acid, **carbohydrates** like sugar and starch, **alcohols** like common (ethyl) alcohol, and **esters** like ethyl acetate and fat. There are also compounds **related to cyanogen,** like prussic acid, which contain nitrogen. We can discuss only one or two examples from each of the groups named.

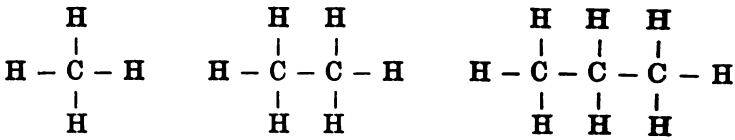
THE HYDROCARBONS.

More than two hundred and fifty compounds of carbon and hydrogen have been described. They fall into several distinct series, the chief one of which contains methane CH_4 as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series.** For the reason that in this series the carbon has all its four valences employed, the members are also called the **saturated hydrocarbons.**

Paraffin Series of Hydrocarbons. — The **names** and **formulæ** of some of the members of the series are:

Gases: methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10} (b.-p. 1°).
Liquids: pentane C_5H_{12} (b.-p. 35°), hexane C_6H_{14} (b.-p. 71°), heptane C_7H_{16} (b.-p. 99°), ...
Solids: hexadecane $C_{16}H_{34}$ (m.-p. 18°), pentatriacontane $C_{35}H_{72}$ (m.-p. 74.7°), hexacontane $C_{60}H_{122}$ (m.-p. 102°).

In composition, each is related to the preceding one by containing the additional units CH_2. Their relations will be more clearly perceived if we employ the graphic formulæ for the first three members. The hydrogen is univalent, and the carbon quadrivalent:



The **natural gas** of Pennsylvania and Ohio contains a large proportion of methane.

Petroleum consists of a mixture of the liquid and solid members of the series in varying proportions, and is found in many parts of the United States, in Ontario, at Baku on the Caspian, in India, and in Japan. In oil-refining, advantage is taken of the differences in the boiling-points to make a partial separation of the components by **fractional distillation.** In this operation a thermometer immersed in the vapor (Fig. 14, p. 26) rises steadily as the less volatile components increase in quantity and the more volatile decrease. The receiver is changed as certain temperatures are reached.

Name.	Components.	B.-P.	Uses.
Petroleum ether	Pentane, hexane	40° – 70°	Solvent, gas-making
Gasolene . . .	Hexane, heptane	70° – 90°	" "
Naphtha . . .	Heptane, octane	80° –120°	" fuel
Benzine . . .	Octane, nonane	120° –150°	"
Kerosene . .	Decane, hexadecane	150° –300°	Illuminating-oil

The portions of still higher boiling-point are used as lubricating oils. **Vaseline** consists of substances $C_{22}H_{46}$ to $C_{23}H_{48}$ (m.-p. 40–50°).

By cooling the residues from the retorts with a freezing mixture (*cf.* p. 204), some of the solid members of the series, $C_{22}H_{46}$ to $C_{28}H_{58}$, are obtained as white flakes, which are separated by filtration in presses. This material forms the **paraffin** used in waterproofing paper, in laundry work, and as an ingredient in candles.

The hydrocarbons are extremely indifferent in their **chemical behavior.** They have none of the properties of acids, bases, or salts. The halogens, notably chlorine and bromine, however, interact with them (see below). When burned they all produce carbon dioxide and water.

Methane CH_4. — Methane, otherwise known as **marsh-gas,** is the chief component of natural gas. It also rises to the surface when

the bottoms of marshy pools are disturbed, and issues from seams in coal beds ("fire-damp" from Ger. *Dampf*, vapor). In these two cases it results from the decomposition of vegetable matter in absence of air.

Methane may be made from inorganic materials by the action of water upon aluminium carbide, prepared by the interaction of aluminium oxide and carbon in the electric furnace (*cf.* pp. 304, 321):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4.$$

In the laboratory the gas is commonly obtained by the distillation of a dry mixture of sodium acetate and sodium hydroxide:

$$NaC_2H_3O_2 + NaOH \rightarrow Na_2CO_3 + CH_4.$$

When a mixture of methane and chlorine is exposed to sunlight several changes occur in succession (*cf.* p. 115):

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl, \qquad CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl,$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl, \qquad CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl.$$

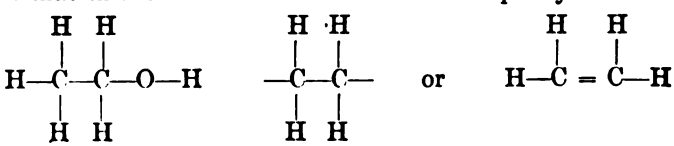
This kind of interaction with the halogens is characteristic of compounds of hydrogen and carbon. It takes place slowly, and is therefore entirely different from ionic chemical change. It consists in a progressive *substitution* of chlorine for hydrogen, unit by unit. **Chloroform** $CHCl_3$ is the only one of the four products which is a familiar substance. The corresponding iodine derivative, **iodoform** CHI_3 is used in surgical dressing. These substances are not salts, and are not ionized in solution. They are very slowly hydrolyzed by water, — carbon tetrachloride, for example, giving carbonic acid and hydrochloric acid.

Ethylene C_2H_4. — Ethylene is the first member of the second series of hydrocarbons. It corresponds to ethane C_2H_6, but contains in each molecule two hydrogen units less than does this substance.

Ethylene is made by heating common alcohol (ethyl alcohol) with concentrated sulphuric acid:

$$C_2H_5OH \rightarrow H_2O + C_2H_4\uparrow.$$

A comparison of the graphic formulæ of the alcohol and ethylene shows that this loss of water leaves the carbon partly unsaturated:



The water may also be removed by allowing alcohol to fall drop by drop into heated phosphoric acid.

Ethylene is formed, along with acetylene and other substances, when any saturated hydrocarbon is heated strongly. Even methane gives it:

$$2CH_4 \rightarrow C_2H_4 + 2H_2.$$

Ethylene is a gas. It burns in the air with a flame which, on account of the great separation of free carbon which takes place temporarily during the combustion (*cf.* Flame), is highly luminous. It will be seen that, in the formula, but three of the valences of each carbon unit are occupied: the substance is unsaturated. Hence, when ethylene is passed through liquid bromine it is rapidly absorbed, and the bromine seems to increase in volume and finally loses all its color, being converted into a transparent liquid having the composition $C_2H_4Br_2$, **ethylene bromide.**

Acetylene.—This substance, likewise a gas, is the first member of still another unsaturated series. Its formula C_2H_2 shows that its molecule lacks four of the hydrogen units necessary to the complete saturation which we find in ethane. Graphically its structure is usually represented thus: $H - C \equiv C - H$. This gas is formed in small quantities by direct union of carbon and hydrogen in the electric arc (p. 320). It is also produced when ethylene is passed through a heated tube: $C_2H_4 \rightarrow C_2H_2 + H_2$ (*cf.* Flame). When calcium carbide (p. 321) is thrown into water it is hydrolyzed. Violent effervescence occurs, the calcium carbide is disintegrated, a precipitate of calcium hydroxide is formed, and acetylene passes off as a gas:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2.$$

This action is like that of water on calcium phosphide (p. 307), and magnesium nitride (p. 281).

Acetylene burns with a flame which is still more luminous than that of ethylene.

The Acids.

Formic Acid HCO_2H.—The removal of water from formic acid produces carbon monoxide (p. 325). Although we cannot reverse the process and cause carbon monoxide to combine with water, we can make it unite with bases. By passing carbon monoxide over hot sodium hydroxide, we obtain sodium formate, from

which formic acid may be liberated by double decomposition with another acid:

$$CO + NaOH \rightarrow NaCO_2H.$$

This acid is secreted by red ants, and is found in stinging nettles. It is a liquid boiling at 100.1°. The molecule contains two atoms of hydrogen, but the acid is, in fact, monobasic.

Acetic Acid $HC_2H_3O_2$ — This acid is produced in the dry distillation of wood* (p. 318). Large quantities of it are manufactured from dilute alcohol. The liquid is allowed to flow in a slow stream through a barrel filled with shavings. Holes in the barrel provide for the access of air, and a bacterium with which the shavings are infected promotes oxidation of the alcohol:

$$C_2H_5OH + O_2 \rightarrow C_2H_3OOH + H_2O.$$

Oxygen alone does not affect alcohol in the cold. The bacterium (*B. aceti*, " mother-of-vinegar ") assists this action, as lower organisms are found to assist many chemical actions, in a way which may be described roughly as catalytic (see Fermentation, p. 332).

The dilute solution of acetic acid produced in this manner contains from five to thirteen per cent of acetic acid, and is known as **vinegar**. By fractional distillation the solution may be concentrated until a little water only remains, and finally, by freezing (*cf.* p. 204), the acetic acid may be crystallized out. Pure acetic acid, in consequence of its freezing readily in cold weather, is known as " glacial " acetic acid. It melts at 16.7° and boils at 118°.

Although four atoms of hydrogen are contained in its molecule, but one of these is replaceable by metals. This fact is recognized in the reaction formula (p. 83) of the acid, $HC_2H_3O_2$.

Oxalic Acid $H_2C_2O_4$. — This acid is dibasic. Its calcium salt CaC_2O_4 is the least soluble of the salts of calcium, and is found in many plants in the form of bundles of needle-shaped crystals. The acid may be made by oxidation of sugar with nitric acid. The white crystalline hydrate, $H_2C_2O_4,2H_2O$, is the form used in the laboratory.

* The dry distillation of bones (p. 318), on the other hand, and of animal matter (p. 281) in general, gives alkaline liquids, because of the ammonia that is formed.

Carbohydrates and Fermentation.

Carbohydrates. — The various kinds of sugar, starch, and cellulose form a closely related group of substances. As it happens that the proportion of hydrogen to oxygen in the composition of most of them is the same as that of these elements in water, they are known by the name of *carbohydrates*. None of these substances show any distinct evidence of ionization.

Dextrose, otherwise known as **glucose** or **grape-sugar,** is a white crystalline substance having the composition $C_6H_{12}O_6$. It is found dissolved in the juices of sweet fruits, such as grapes.

The most familiar sugar is **cane-sugar** $C_{12}H_{22}O_{11}$, which may form as much as 18 per cent by weight of the juices pressed from the sugar-cane, and sometimes reaches 16 per cent of the fluid material in the sugar-beet. It is prepared by boiling the juices with animal charcoal (p. 319), to remove the coloring matter which would otherwise give the sugar a brown tint. The liquid is then concentrated until crystals appear. The mother-liquor which no longer deposits crystals is known as *molasses*.

The relation of **starch** to the sugars is seen, not only in the formula $(C_6H_{10}O_5)_n$, but in the fact that by boiling starch with dilute acids, dextrose is formed along with other products of the hydrolysis. Commercial "glucose" is made by this process. Starch is an insoluble white substance which is found in the form of fine particles in the fruit and other parts of plants.

Cellulose has the same composition as starch. It forms the framework of the cells of plants. In many cases it is overlaid with a considerable thickness of lignin, which in **paper-making** is removed by boiling the wood with sodium hydroxide or calcium bisulphite solution (p. 266). When the product has been washed thoroughly with water, almost pure cellulose remains. Matted cellulose in thin sheets forms the basis of paper, and filter paper contains nothing else (see under Aluminium sulphate). Other forms of pure cellulose are known as cotton, linen, and jute, according to their sources. Although the chemical composition of these varieties is identical, the physical properties vary considerably.

Fermentation. — This is the name given to a number of different chemical changes, brought about by catalytic action of complex

chemical compounds secreted by living organisms. These compounds are called **enzymes**, and, in many cases, have been separated from the organisms by means of solvents. Their action must be regarded as catalytic, since small quantities of the active organisms or of the enzymes can produce very extensive chemical changes without themselves suffering alteration in the process.

The organisms may be divided into three classes, each secreting different enzymes which confine themselves for the most part to special kinds of chemical change. (1) The **molds**, when grown in sugar solution or beef extract, or other nutritive solutions, produce decompositions known collectively as putrefaction. (2) **Certain bacteria** promote the oxidation of alcohol to acetic acid (p. 331). Some also decompose sugar, furnishing butyric or lactic acid as one of the products. (3) The **yeasts** (*saccharomycetes*) flourish in solutions of some sugars, and decompose them into alcohol and carbon dioxide. This decomposition is known as alcoholic fermentation. These changes are usually brought about by actual introduction of the organism. In brewing, however, the enzyme itself, diastase, is employed to hydrolyze starch.

When yeast is added to a solution of cane-sugar, hydrolysis into dextrose and levulose first occurs:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

This change is produced also by boiling with dilute acids. But the enzyme of the yeast immediately decomposes the dextrose and the levulose into alcohol and carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

The liquid effervesces, and the carbon dioxide escapes into the air.

Alcohols, Esters, and Soap.

Alcohols.—When wood is distilled (p. 318), **methyl alcohol** CH_3OH is found in the fluid product. When purified this is a colorless liquid boiling at 66°. Its solution in water shows no evidence of ionization.

Common or **ethyl alcohol** C_2H_5OH is formed in the fermentation of solutions of sugar by yeast (p. 333), and is separated from the water and the other products of fermentation by distillation. The product contains 95% of alcohol by volume (in Great Britain, 90%) and is

applicable to most commercial uses. Absolute alcohol, entirely free from water, is made by placing the spirit in vessels filled with quicklime. The latter interacts with the water producing calcium hydroxide, and the clear liquid which is poured off is distilled once more. Pure alcohol boils at 78.3°.

Glycerine $C_3H_5(OH)_3$ is an alcohol containing three hydroxyl groups, — a trihydric alcohol.

Esters: Soap. — When an acid and an alcohol are mixed, an **ester** and water are formed. The action is slow and, being reversible, is always incomplete. But by introduction of a dehydrating agent, like concentrated sulphuric acid, the water is removed and the change brought to completion. Thus, ethyl alcohol and acetic acid, when warmed with sulphuric acid, give **ethyl acetate**:

$$C_2H_5OH + HC_2H_3O_2 \rightleftarrows C_2H_5C_2H_3O_2 + H_2O.$$

When this, or any other ester, is boiled with excess of water, the foregoing action is reversed.

When esters are boiled with strong bases, such as sodium hydroxide solution, an alcohol and the salt of the acid are formed:

$$NaOH + C_2H_5C_2H_3O_2 \rightarrow C_2H_5OH + NaC_2H_3O_2.$$

The **fats** are mixtures of complex esters and undergo this change just as do the simpler esters. The sodium salts produced from fats are known as **soaps**, and this general kind of action is called, therefore, **saponification** (Lat. *sapo*, soap).

In beef fat the chief esters present are tripalmitin, tristearin, and triolein. It will be sufficient to illustrate the chemistry of the manufacture of **soap** by discussing the case of one of these substances. Tripalmitin is the glyceryl ester of palmitic acid. When fat is mixed with hot sodium hydroxide solution it first forms an emulsion* in which the fat is disseminated in minute droplets through the liquid. This is a result of surface tension. When the emulsion is boiled, the fat is slowly decomposed into glycerine and sodium palmitate. The change is similar in plan to the simpler one just discussed:

$$3NaOH + C_3H_5(C_{16}H_{31}O_2)_3 \rightarrow C_3H_5(OH)_3 + 3NaC_{16}H_{31}O_2.$$

* In the intestines the same office is performed by the gall, secreted by the liver, and so the fat is prepared for absorption into the system.

Changes similar to this occur with the other two esters. The only difference is that the organic radical in the case of tristearin is $C_{18}H_{35}O_2$, and in the case of triolein $C_{18}H_{33}O_2$. Both products in each of the three cases are soluble in water, but when common salt is added to the solution the sodium salts of the organic acids are separated (" salted out ") as a solid mass, which is known as soap. When potassium hydroxide takes the place of sodium hydroxide the whole unsalted mass is semi-fluid, and is known as soft soap.

The components of soap, like other soluble salts, are highly ionized in solution, and show all the properties of ionogens. For example, addition of an acid liberates the organic acid. So also, when soap is dissolved in hard water (*cf.* p. 77), a white, flocculent precipitate is formed, which coagulates upon the sides of the vessel. This is a mixture of the calcium salts formed by union of the proper ions. For example, the sodium palmitate is changed as follows:

$$2NaC_{16}H_{31}O_2 + CaSO_4 \rightarrow Ca(C_{15}H_{31}COO)_2\downarrow + Na_2SO_4.$$

Most of the salts of these acids, with the exception of those of potassium and sodium, are insoluble in water.

Cyanogen.

Cyanogen C_2N_2. — This compound is prepared by allowing a solution of cupric sulphate to trickle into a warm solution of potassium cyanide. The cupric cyanide, at first precipitated, quickly decomposes, giving cuprous cyanide and cyanogen:

$$2KNC + CuSO_4 \rightarrow Cu(NC)_2\downarrow + K_2SO_4,$$
$$2Cu(NC)_2 \rightarrow 2CuNC + C_2N_2\uparrow.$$

Cyanogen is a very poisonous gas with a characteristic, faint odor.

Hydrocyanic Acid HNC. — This acid, called also **prussic acid**, is most easily made by the action of an acid upon a cyanide (see Potassium cyanide) followed by distillation. It is a colorless liquid boiling at 26.5°. It has an odor like that of bitter almonds, and is highly poisonous. In aqueous solution it is an extremely feeble acid. Hydrocyanic acid and the cyanides are unsaturated compounds, a fact which is illustrated in the two following paragraphs.

Cyanates and Thiocyanates. — When potassium cyanide is fused and stirred with an easily reducible oxide, like lead oxide

(PbO), the metal (for example, the lead) collects at the bottom of the iron crucible in molten form, and **potassium cyanate** KNCO is produced:

$$KNC + PbO \rightarrow KNCO + Pb.$$

When potassium cyanide in aqueous solution is boiled with sulphur or with a polysulphide (p. 255), it is converted into **potassium thiocyanate** KCNS. This salt, or **ammonium thiocyanate** NH_4CNS, is used in testing for ferric ions on account of the deep-red color of ferric thiocyanate (*cf.* p. 179).

Exercises. — 1. Make the graphic formulæ of hexane (p. 327), ethyl formate, ethylene bromide (p. 330), ethyl alcohol.

2. Make equations for the formation of aluminium carbide (p. 329), the saponification of triolein (p. 334).

3. Prepare a **summary** of the various statements that have been made in the text about **catalysis** (*e.g.* pp. 54, 74, 110, 114, 161, 257, 268, 302, 333), and illustrate fully.

CHAPTER XXX

FLAME AND ILLUMINANTS

Meaning of the Term. — In the combustion of charcoal there is hardly any **flame**, for the light emanates almost entirely from the incandescent, massive solid. When two gases are mixed and set on fire, a sort of flame passes through the mixture, but this can hardly be accounted a flame, in the ordinary sense, either. The rapid movement of the flash, and the explosion which accompanies it, are in a manner the precise opposite of the quiet combustion which is characteristic of flames.

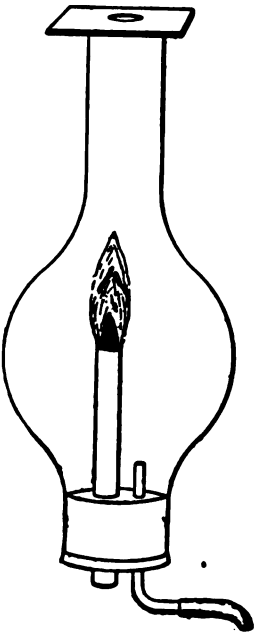


FIG. 60.

With illuminating-gas the production of its very characteristic flame is due to the chemical union of a stream of one kind of gas in an atmosphere of another. The flame is made up of the heated matter where the two gases meet. In the case of a burning candle, one of the bodies appears to be a solid, but a closer scrutiny of the phenomenon shows that the solid does not burn directly. A combustible gas is manufactured continuously by the heat of the combustion and rises from the wick. The introduction of a narrow tube into the interior of the flame enables us to draw off a stream of this gas and to ignite it at a remote point. Thus, **a flame is a phenomenon produced at the surface where two gases meet and undergo combination with the evolution of heat and, more or less, light.**

In the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists

of substances ordinarily known as combustibles, or whether this order is reversed. In an atmosphere of ordinary illuminating-gas, the flame must be fed with air. This condition is easily realized (Fig. 60). The lamp-chimney is closed at the top until it has become filled with illuminating-gas. After the lapse of a few minutes this can be ignited as it issues from the bottom of the wide, straight tube which projects from the interior. When the hole in the cover of the lamp-chimney is then opened, the upward draft causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal-gas. In an atmosphere of this kind, materials playing the part of a candle burning in air would have to be substances which, under the influence of the heat of combustion, give off oxygen. Strongly heated potassium chlorate, for example, appears to burn continuously in such an atmosphere when lowered into it in a deflagrating spoon.

Luminous Flames. — The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (*cf.* p. 74) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some incandescent solid.

In the Welsbach lamp the flame itself is non-luminous, and, but for the mantle, would be identical with the ordinary Bunsen flame. The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide (ThO_2) and one per cent cerium dioxide (CeO_2). While many cheaper oxides would give out a white light, they have neither sufficient coherence, nor sufficiently lasting, high emissivity to make their use practicable. It is worth noting that any appreciable variation from the above proportions, by the introduction of either more or less cerium oxide, produces a marked diminution in the intensity and whiteness of the light.

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating-gas does not at first sight

appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas. Carbon is, indeed, an extremely combustible substance, and is eventually entirely consumed. But a fresh supply is continually being generated in the interior of the flame, while the oxygen with which it is to unite is outside the flame altogether. Thus the carbon particles persist until, drifting with the spreading gas, they reach the periphery of the flame.

The Bunsen Flame.— In the burner devised by Robert Bunsen, a jet of ordinary illuminating-gas is projected from a narrow opening into a wider tube. In this tube it becomes mixed with air, drawn in through openings whose dimensions can be altered by means of a perforated ring. When the supply of air is sufficient, the flame becomes non-luminous. With a somewhat different construction, and the use of a bellows to force a larger proportion of air into the gas, a still hotter flame can be produced. The instrument in this case is known as a blast-lamp. The high temperature of the Bunsen flame is not difficult to account for. It will be seen at once, on handling the burner, that the flame diminishes to one-half or one-third of its previous size when air is admitted. Since the same amount of gas is burning in both cases, and the products in both cases are water and carbon dioxide, the total amounts of heat produced must in both cases be the same. The production of an equal amount of heat in a smaller flame necessarily causes this to have a higher average temperature.

Structure of the Illuminating and the Bunsen Flame.— When an exceedingly small luminous flame is examined, the various parts of which it consists may easily be made out. In the interior there is a dark cone which is composed of illuminating-gas and air, and in it no combustion is taking place. A match-head may be held here for some time without being set on fire. This is therefore not properly a part of the flame. Outside this is a vivid blue layer (*C*, Fig. 61) which is best seen in the lower part of the flame, but extends beneath the luminous sheath, and covers the dark inner cone completely. Outside the blue flame, and covering the greater part of

it, is the cone-shaped luminous portion (*B*). Over all is a faint mantle of non-luminous flame (*A*), which becomes visible when the light from the luminous part is purposely obstructed. In the luminous gas-flame, therefore, there are four regions, if we count the inner cone of gas. The difference between this and the non-luminous Bunsen flame is that in the latter the luminous region is omitted, and the inner, dark cone, the blue sheath, and the outer mantle, are the only parts which can be distinguished.

FIG. 61.

Illuminating-Gas and its Composition. — Before considering the chemistry of the gas-flame, it is necessary to know what substances are burning. The illuminating-gas in Europe, and in many of the smaller cities of the United States, is usually coal-gas, while in the larger cities of America it is almost always made from water-gas. **Coal-gas** is obtained by the destructive distillation of soft coal, and is freed from ammonia (*cf.* p. 281) and tar by washing and cooling, and from hydrogen sulphide and carbon dioxide by passage through layers of slaked lime. The **water-gas**, made by the action of steam upon anthracite or coke, being composed of carbon monoxide and hydrogen (*cf.* p. 325), has no illuminating power. It is therefore "carburetted," that is, mixed with hydrocarbons, by passage through a cylindrical structure filled with white-hot firebrick, upon which falls a small stream of high-boiling petroleum. The relatively involatile hydrocarbons of which the oil consists are thus decomposed (" cracked "), and gaseous substances of high illuminating power are produced. The following table shows the composition of each of these kinds of gas, together with that of oil-gas (Pintsch's), which is composed entirely of the products from " cracking " oil:

Components.	Coal-Gas.	Water-Gas.	Oil-Gas.
Illuminants	5.0	16.6	45.0
Heating gases:			
Methane	34.5	19.8	38.8
Hydrogen	49.0	32.1	14.6
Carbon monoxide . .	7.2	26.1	. . .
Impurities:			
Nitrogen	3.2	2.4	1.1
Carbon dioxide . . .	1.1	3.0	. . .
Candle power	17.5	25.0	65.0

These are average numbers, and considerable variations from these proportions are often met with. The illuminants are unsaturated hydrocarbons, such as ethylene and acetylene, and the value of the gas for illuminating purposes depends on the amount of these particular components.

The Causes of Luminosity and Non-Luminosity. — The study of the chemical changes taking place in the Bunsen flame, particularly with the object of explaining (1) the luminosity of the flame of the pure gas, and (2) the non-luminosity of that produced by the same gas when it is mixed with air, has been the subject of many elaborate investigations. The questions are: (1) Why is carbon liberated in the former case, and (2) why is it not liberated in the latter? Let us consider these questions in order.

1. The investigations referred to show conclusively that the free carbon in the luminous zone of the ordinary flame is accompanied by free hydrogen, and that both are formed by dissociation of the ethylene. This substance, when heated, gives acetylene, and the latter then dissociates into carbon and hydrogen (p. 330):

$$C_2H_4 \rightarrow H_2 + C_2H_2 \rightarrow 2C + H_2.$$

The carbon glows, until, as it drifts outwards, it encounters the oxygen of the air and is burned. That carbon glows when heated in the absence of oxygen, without being consumed, is a fact familiar in the behavior of the incandescent electric lamp, the filament of which is made of carbon.

The conception that when hydrocarbons burn, they first undergo dissociation, and then union with oxygen, is in harmony with what we have observed also in the case of the combustion of hydrogen sulphide, where the presence of free sulphur and free hydrogen in the interior of the flame was demonstrated (p. 251).

2. The influence of the air admitted to the Bunsen burner, in interfering with this dissociation in such a way as to destroy all luminosity, is the most difficult point to explain. The effect is frequently attributed to the oxygen which the air contains. This view, however, is seriously weakened by a consideration of the undoubted fact that oxygen is not required. Carbon dioxide and steam are equally efficient when introduced instead of air. Even nitrogen, which cannot possibly be suspected of furnishing any oxygen, like-

wise destroys the luminosity. Lewes has shown that 0.5 volumes of oxygen in 1 volume of coal-gas destroy the luminosity. But 2.30 volumes of nitrogen or 2.27 volumes of air accomplish the same result. Thus the efficiency of air is not much greater than that of nitrogen, in spite of the fact that one-fifth of the former is oxygen.

It is evident that the effect is due, in part at least, to the *dilution* with a *cold* gas. This is confirmed by the observation that a cold platinum dish held in a small luminous flame is similarly destructive of the luminosity. If the tube of the Bunsen burner is heated so that the mixed gases are considerably raised in temperature before reaching the non-luminous flame, the latter becomes luminous. It is probable, therefore, that the cold gas lowers the temperature of the inner flame, and at the same time the dilution diminishes the speed with which the free carbon is formed (Lewes). Even if the temperature is not reduced below that at which dissociation of the ethylene can occur, yet the dilution and cooling, together, prevent that sharp dissociation at this particular point which is necessary for the production of the great excess of free carbon needed to furnish the light.

Exercises.— 1. In what way will calcium hydroxide remove hydrogen sulphide from coal-gas (p. 340)?

2. Make a section showing the shape of the flame produced by burning hydrogen gas when the latter issues from a circular opening.

CHAPTER XXXI

SILICON AND BORON

In respect to **chemical relations** there is a close resemblance between silicon and carbon. The former element gives no monoxide, however, and is quadrivalent in all its compounds. In chemical character it is strictly non-metallic.

Occurrence. — Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand (SiO_2), and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

Preparation of Silicon. — When finely powdered magnesium and sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:

$$2Mg + SiO_2 \rightarrow Si + 2MgO.$$

At the same time, and especially if excess of the metal is used, some magnesium silicide Mg_2Si is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide, and leaves the **silicon (amorphous)** undissolved. When amorphous silicon is dissolved in molten zinc, the mass, after solidification, is found to contain **crystalline silicon.** The zinc is removed by the action of a dilute acid, the silicon remaining unaffected.

Properties. — **Amorphous silicon** is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at 430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is slowly oxidized by *aqua regia* to silicic acid, and is dissolved by a mixture of

hydrofluoric acid and nitric acid, giving silicon tetrafluoride. **Crystallized silicon** consists of black needles belonging to the hexagonal system. Its chemical behavior is like that of the amorphous variety just described.

Both kinds of silicon act upon boiling solutions of potassium or sodium hydroxide (*cf.* p. 67), the ortho- or metasilicate being formed:

$$Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2.$$

Silicon Hydride SiH_4. — Silicon differs from carbon in giving only two well-defined compounds with hydrogen. The chief one may be liberated as a gas by the action of hydrochloric acid upon magnesium silicide:

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4.$$

The action is similar to that by which hydrogen sulphide is made. The pure gas is easily inflammable, and unites with oxygen to form water and silicon dioxide. When heated alone, it decomposes into its constituents.

Carbide of Silicon SiC. — This compound is manufactured for use as an abrasive, and is sold under the name of **carborundum**. A mixture of quartz-sand, coke, and common salt is heated to about 3500° in the electric furnace:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

Silicon carbide when pure is composed of transparent, colorless, hexagonal plates. Ordinarily the crystals are brown or black. It stands next to the diamond and carbide of boron in hardness. It is used in making machinery for polishing hard rock, such as granite, and is employed also for protecting the walls of puddling furnaces (*q.v.*), and in other ways in the steel industry.

Silicon Tetrachloride and Tetrafluoride. — The tetrachloride $SiCl_4$ is formed by direct union of the free elements. It is more conveniently prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon. The gaseous products enter a condenser in which the tetrachloride assumes the liquid form:

$$2Cl_2 + SiO_2 + 2C \rightarrow SiCl_4 + 2CO.$$

Chlorine is unable to displace oxygen from combination with silicon, and has, therefore, when alone, no effect upon sand. In the above

action, therefore, the carbon is used to secure the oxygen while the chlorine combines with the silicon. This kind of interaction is in some degree different from any which we have hitherto encountered. It bears no special name, but the principle underlying it is very commonly employed (see, *e.g.*, Chlorides of boron and aluminium).

Silicon tetrachloride is a colorless liquid (b.-p. 59°) which fumes strongly in moist air, and acts violently upon cold water, giving silicic acid:

$$SiCl_4 + 4H_2O \rightarrow 4HCl + Si(OH)_4\downarrow.$$

When strong hydrofluoric acid acts upon sand, **silicon tetrafluoride** SiF_4 is liberated:

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4.$$

Since the water interacts with the tetrafluoride (see below), the latter is usually made by heating sand with powdered calcium fluoride and excess of sulphuric acid. In this way the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid renders the water inactive. Hydrofluoric acid acts in a corresponding way upon all silicates (*q.v.*), whether these are minerals or are artificial silicates like glass (*cf.* p. 171).

Silicon tetrafluoride is a colorless gas. It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:

$$\begin{array}{rl} SiF_4 + 4H_2O \rightarrow Si(OH)_4\ (+\ 4HF) & (1) \\ (4HF) + 2SiF_4 \rightarrow 2H_2SiF_6 & (2) \\ \hline 3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6 & \end{array}$$

The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of **hydrofluosilicic acid.**

Hydrofluosilicic Acid H_2SiF_6. — This acid is stable only in solution. When the water is removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when they are heated. This acid is used in analysis chiefly because its potassium and sodium salts are amongst the few salts of these metals which are relatively insoluble in water. The barium salt is also insoluble, but most of the salts of the heavy metals are soluble.

Silicon Dioxide SiO_2. — This substance may be made in the form of a fine white powder by heating precipitated silicic acid. It is found in many different forms in nature. In large, transparent, six-sided prisms with pyramidal ends it is known as **quartz** or **rock crystal**. When colored by manganese and iron it is called **amethyst**, when by organic matter, **smoky quartz**. A special arrangement of the structure gives **cat's eye**. Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate**, **jasper**, and **onyx**, the last much used in making cameos. Slightly hydrated forms of silica are the **opal** and **flint**.

Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with potassium hydroxide solution it forms potassium meta- or orthosilicate:

$$SiO_2 + 4KOH \rightarrow K_4SiO_4 + 2H_2O.$$

The salt is left as a gelatinous solid (" soluble glass ") when the water is evaporated. The silicates of potassium and sodium may also be obtained by boiling sand with the carbonates of these metals, carbon dioxide being displaced. They are produced more rapidly, however, usually as metasilicates (see below), by *fusing* the sand with the alkali carbonates:

$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2.$$

Silica is found in the hard parts of straw, of some species of horsetail (*equisetum*), and of bamboo. In the form of whetstones it is used for grinding. The clear crystals are employed in making spectacles and optical instruments. Pure sand is used in glass manufacture (*q.v.*). Recently, small pieces of chemical apparatus have been manufactured by fusing quartz in the oxyhydrogen flame or the electric furnace. Owing to the low coefficient of expansion of silica, the vessels fashioned out of it can be heated or cooled as suddenly as we choose, without risk of fracture.

Silicic Acid H_4SiO_4 — When acids are added to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. When, however, the silicate is poured into excess of hydrochloric acid, no precipitation occurs. The

silicic acid remains in **colloidal solution** (a form of very fine suspension). The acid before precipitation is probably orthosilicic acid:

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + Si(OH)_4,$$
$$Na_2SiO_3 + 2HCl + H_2O \rightarrow 2NaCl + Si(OH)_4,$$

but the gelatinous precipitate, when dried, contains a smaller proportion of the elements of water. There seem to be no definite stages, indicating the existence of various acids, such as we observe with phosphoric acid. The final product of drying is the dioxide.

Silicic acid is a very feeble acid, and, therefore, gives no salt with ammonium hydroxide. The potassium and sodium salts give strongly alkaline solutions (*cf.* pp. 254, 324).

Silicates. — While silicic acid is presumed to be the ortho-acid $Si(OH)_4$, and no other silicic acids have been made, the salts are most easily classified by imagining them to be derived from various acids representing different degrees of hydration of the dioxide (*cf.* p. 310), or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:

$$H_4SiO_4 - H_2O \rightarrow H_2SiO_3 \ (= H_2O,SiO_2) \quad \text{Metasilicic acid.}$$
$$\left.\begin{array}{l} 2H_4SiO_4 - H_2O \rightarrow H_6S_2O_7 \ (= 3H_2O,2SiO_2) \\ 2H_4SiO_4 - 3H_2O \rightarrow H_2Si_2O_5 \ (= H_2O,2SiO_2) \end{array}\right\} \text{Disilicic acids.}$$
$$3H_4SiO_4 - 4H_2O \rightarrow H_4Si_3O_8 \ (= 2H_2O,3SiO_2) \quad \text{Trisilicic acid.}$$

Di- and trisilicates are those derived from acids containing two and three units of silicic anhydride, respectively, in the formula. The valences of the radicals of the acids are shown by the number of hydrogen units in the formulæ.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them mixed salts (p. 231) are very common, in which the hydrogen of the imaginary acid is displaced by two or more metals in such a way that the total quantity of the metals is equivalent to the hydrogen. The following list presents in tabular form some **typical or common minerals** arranged according to the foregoing classification:

Orthosilicates (H_4SiO_4)	Zircon, $ZrSiO_4$ Mica, $KH_2Al_3(SiO_4)_3$ Kaolin, $H_2Al_2(SiO_4)_2.H_2O$
Metasilicates (H_2SiO_3)	Wollastonite, $CaSiO_3$ Beryl, $Gl_3Al_2(SiO_3)_6$ Talc, $H_2Mg_3(SiO_3)_4$
Disilicate ($H_6S_2O_7$)	Serpentine, $Mg_3Si_2O_7$,
Trisilicate ($H_4Si_3O_8$)	Orthoclase (feldspar), $KAlSi_3O_8$

It will be seen that the total valence of the metal units is equal to that of the acid radicals. Thus, in beryl there are six equivalents of glucinum (beryllium) and six of aluminium, taking the place of twelve units of hydrogen in $(H_2SiO_3)_6$.

Mica, which is obtained in large sheets from Farther India, is used in making lamp-chimneys and as an insulator in electrical apparatus. **Kaolin**, or **clay**, like mica, is an acid orthosilicate.

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** is a more or less coarse mixture of quartz, mica, and feldspar. Frequently the oblong, flesh-colored or white crystals of the last are large and very conspicuous. **Sandstone** is composed of sand cemented together by clay or by lime, and colored brown or yellow by ferric oxide.

Boron B.

As regards **chemical relations**, boron, being a uniformly trivalent element, is a member of the aluminium family (see Table of periodic system, at the end of this book). Yet it is a pronounced non-metal, and its oxide and hydroxide are acidic: aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties, except the property of valence.

Occurrence. Like silicon, boron is found in oxygen compounds, namely, in boric acid (*q.v.*) and its salts. Of the latter, sodium tetraborate $Na_2B_4O_7$, or borax, came first from India under the name of tincal. In constitutes a large deposit in Borax Lake in California. Colemanite, $Ca_2B_6O_{11}.5H_2O$, from California, and other complex borates, furnish a large part of the commercial supply of compounds of boron.

Preparation. — When boric oxide is heated with powdered magnesium ($B_2O_3 + 3Mg \rightarrow 3MgO + 2B$), black, amorphous boron can be separated with some difficulty from the borides of magnesium in the resulting mixture. When excess of powdered aluminium is used, hard crystals of boron are formed.

Properties. — Boron unites with the same elements as does silicon (p. 343), but with somewhat greater activity. Like carbon (pp. 257, 299), it is also oxidized by hot, concentrated sulphuric or nitric acid, the product being boric acid. It interacts with fused potassium hydroxide, giving a borate:

$$2B + 6KOH \rightarrow 2K_3BO_3 + 3H_2.$$

Boron, when heated with nitrogen, unites directly to form the **nitride** BN, a white solid. When heated in the electric furnace with carbon, it forms a **carbide** B_6C. This substance is harder than carborundum, and stands next to the diamond in respect to hardness.

The Halides of Boron. — By combined action of carbon and chlorine on boric oxide, using the principle employed in preparing silicon tetrachloride (p. 344), the **trichloride of boron** BCl_3 may be made. It is a liquid (b.-p. 18°) which fumes strongly in moist air, and is completely hydrolyzed by water.

Boron trifluoride BF_3 is made by the interaction of calcium fluoride and sulphuric acid with boron trioxide. The mode of preparation and the properties of the substance recall silicon tetrafluoride (p. 345). It interacts with water, like the latter, giving boric acid and **hydrofluoboric acid** HBF_4:

$$4BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HBF_4.$$

Boric Acid and Boron Trioxide. — Boric acid (boracic acid, H_3BO_3) is somewhat volatile with steam, and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained in basins of brickwork, is placed over the openings, and from this water, after evaporation, boric acid is obtained in crystalline form. As boric acid is very feeble, and withal little soluble, it may also be made by interaction of sulphuric acid and concentrated borax solution:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \leftrightarrows Na_2SO_4 + 4H_3BO_3\uparrow.$$

Boric acid crystallizes from water in thin white plates, which are unctuous (like graphite and talc) to the touch. Its solubility in water

is 4 parts in 100 at 19°, and 34 in 100 at 100°. The solution scarcely affects litmus. It confers a green tint on the Bunsen flame. This behavior is used as a test for the acid. At 100° the acid slowly loses water, leaving metaboric acid HBO_2, and at 140° tetraboric acid is formed: $4HBO_2 - H_2O \rightarrow H_2B_4O_7$. Strong heating gives the trioxide B_2O_3 a glassy, white solid. When dissolved in water, all these dehydrated compounds revert to boric acid. The solution of boric acid in water is used as an antiseptic in medicine, and as a preservative for milk and other foods.

Borates. — Borates derived from orthoboric acid are practically unknown. The most familiar salt is borax or sodium tetraborate. The decahydrate $Na_2B_4O_7,10H_2O$, which crystallizes from water at 27° in large, transparent prisms, and the pentahydrate which crystallizes at 56°, are both marketed. They are made by crystallization of native borax. In Germany, borax is prepared from boracite, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid:

$$MgCl_2,2Mg_3B_8O_{15} + 12HCl + 18H_2O \rightarrow 7MgCl_2 + 16B(OH)_3.$$

The boric acid is redissolved in boiling water, and sodium carbonate is added: $4B(OH)_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$. In California it is made from colemanite by interaction with sodium carbonate.

Since boric acid is a feeble acid, borax is extensively hydrolyzed by water, and the solution has a marked alkaline reaction (*cf.* p. 254).

When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (*cf.* p. 312), and is used in the form of beads in analysis. If its formula be written $2NaBO_2,B_2O_3$ (*cf.* p. 310) it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with blue, from the presence of a compound like $2NaBO_2,Cu(BO_2)_2$. Cobalt compounds give a deep-blue color to the bead.

Exercises. — 1. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

2. What would be the interaction between aqueous solutions of an ammonium salt and of sodium orthosilicate (*cf.* p. 347)?

CHAPTER XXXII

THE BASE-FORMING ELEMENTS

In the present chapter a preliminary view of the chemistry of the metallic elements is given.

Physical Properties of the Metals. — Metals show what is commonly called a **metallic luster**, but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but most of the metals when in this condition are black.

The metals can all be obtained in **crystallized form**, when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system.

The metals vary in **specific gravity** from lithium, which is little more than half as heavy as water (sp. gr. 0.59), to osmium, whose specific gravity is 22.5. Those which have a specific gravity less than 5, namely, potassium, sodium, calcium, magnesium, aluminium, and barium, are called the **light metals**, and the others the **heavy metals**.

Most metals are **malleable**, and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle. The order of the elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in an order different from the above. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. The values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 27, Al 20, Zn 5, Pb 2.

The **hardness** is measured by the ease with which the material may be disintegrated by a sharp, hard instrument. Potassium is as soft as wax, while chromium is hard enough to cut glass.

The **temperature** at which the metal **fuses** has an important bearing

on its manufacture. Most of the following **melting-points** are only approximate:

Mercury . . .	−40°	Zinc	420°	Cast iron	1150°
Potassium . .	62°	Antimony .	437°	Nickel . .	1500°
Sodium . . .	96°	Aluminium .	700°	Iron (pure)	1550°
Tin	230°	Magnesium .	750°	Platinum .	1780°
Bismuth . . .	264°	Silver . . .	954°	Manganese	1900°
Cadmium . .	320°	Copper . . .	1057°	Chromium	2000°
Lead	326°	Gold	1075°	Iridium .	2200°

It will be seen that mercury is a liquid, that potassium and sodium melt below the boiling-point of water, and that the metals down to the foot of the second column can be melted easily with the Bunsen flame.

The methods of manufacture and the treatment of metals are much influenced also by their **volatility**. The following are easily distilled: Mercury, b.-p. 357°; potassium and sodium, b.-p. about 700°; cadmium, b.-p. 770°; zinc, b.-p. 950°. Even the most involatile metals can be converted into vapor in the electric arc.

In many cases molten metals dissolve in one another freely. The results are called **alloys**, and in some cases have the properties of solid solutions. Sometimes, as in the case of lead and tin, mixtures can be formed in all proportions. On the other hand, the solubility may be limited, as in the case of zinc and lead, where only 1.6 parts of the former dissolve in 100 parts of the latter. The colors of alloys are not the average of those of the constituents. Thus, the nickel alloy used in coining contains 75 per cent of copper and 25 per cent of nickel, yet it shows none of the color of the former.

Alloys in which mercury forms one of the components are known as **amalgams** (Gk. *μάλαγμα*, a soft mass), and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The following table gives the conductivities of the metals (expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 15°, offer a resistance of one ohm):

Silver, cast	62.89	Nickel, cast	7.59
Copper, commercial	57.40	Iron, drawn	7.55
Gold, cast	46.30	Platinum	5.7–8.4
Aluminium, commercial	31.52	Steel	5.43
Zinc, rolled	16.95	Lead	4.56
Brass	14.17	Mercury	1.049

To compare these **conductivities** with those of solutions, it may be said that decinormal hydrochloric acid (p. 226) has a conductivity on the above scale of 0.035, or a thirtieth of that of mercury.

General Chemical Relations of the Metallic Elements.— Since most of the compounds of the metals are ionogens, their solutions, except when the metal is a part of a compound ion, all contain the metal in the ionic state, and the resulting substances, such as potassium-ion and cupric-ion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound, are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *dry state* are of importance in connection with metallurgy.

There are **three chemical properties** which are **characteristic of the metallic elements.** The first two of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive* radicals of salts, and, therefore, to exist alone as positive ions (pp. 224, 271).

2. The oxides and hydroxides of the metals are basic (pp. 81, 271).

3. Each *typical* metal has at least one halogen compound which is little, if at all, hydrolyzed by water (p. 272). The same thing is true of nitrates and other salts of active acids.

In reference to the third characteristic, the **non-hydrolysis of halides of typical metals,** a word of explanation is required. **Active bases** (hydroxides of typical metals), such as sodium hydroxide, give, with feeble acids, such as H_2S (p. 253), H_2PO_4' (p. 311), H_2CO_3 (p. 324), H_2SiO_3 (p. 347) and H_3BO_3 (p. 350), salts whose solutions are **alkaline in reaction.** This is due to hydrolysis. But **active bases** give with **active acids,** such as HCl, and HNO_3, salts whose solutions are **neutral in reaction.** This is the fact expressed in the third characteristic of the metallic elements. The **less active bases,** being hydroxides of less active metallic elements, give, with active acids, salts whose solutions are not neutral, but **acid in reaction.** Thus cupric chloride

solution is feebly acid. This is because there is a tendency for the ions of the water to form the slightly dissociated molecules of the base:

$$Cu^{\cdot\cdot} + 2OH' + 2H^{\cdot} \rightarrow Cu(OH)_2 + 2H^{\cdot}.$$

Finally, a salt derived from a **base and an acid**, both of which are **weak** is also hydrolyzed, often completely. Aluminium carbonate and ammonium silicate (p. 347) are examples of salts which, for this reason, are completely hydrolyzed. The resulting mixture may have an acid or a basic reaction, if the acid or the base is sufficiently soluble and sufficiently active. Thus, ammonium sulphide solution is alkaline.

Aside from these points, many features in the behavior of metals and their compounds are summed up in the electromotive series (p. 245). The reader should re-read all the parts referred to above before proceeding farther. He should also reëxamine the various kinds of chemical changes discussed on pp. 124, 163, 189 and particularly the varieties of ionic chemical change on p. 243.

Occurrence of the Metals in Nature. — The minerals from which metals are extracted are known as **ores**. They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature it is said to be **native**. Thus we have gold, silver, metals of the platinum group, copper, mercury, bismuth, antimony, and arsenic occurring native (*cf.* p. 245).

The metals whose **oxides** are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose **sulphides** are used as ores are nickel, cobalt, antimony, lead, cadmium, zinc, and copper.

From the **carbonates** we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, strontium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as **sulphates** are those whose sulphates are not freely soluble, namely, lead, barium, strontium, and calcium.

Compounds of metals with the **halogens** are not so numerous.

Silver chloride furnishes a limited amount of silver. Sodium and potassium chlorides are found in the salt-beds, and cryolite $3NaF, AlF_3$ is used in the manufacture of aluminium.

The natural **silicates** are very numerous, but are seldom used for the preparation of the metals. Many of them are employed for other commercial purposes, kaolin (p. 348) being a conspicuous example of this class.

Methods of Extraction from the Ores. — The art of extracting metals from their ores is called **metallurgy**. Where the metal is **native**, the process is simple, since melting away from the matrix (p. 248) is all that is required. Frequently a **flux** is added. A flux usually is a substance which interacts with infusible materials to give fusible ones. It combines with the matrix, giving a fusible **slag**. Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a compound, the metal has to be liberated by our furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper, for example. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. This procedure has received the name **aluminothermy** (*q.v.*) on account of the great amounts of heat liberated. In the laboratory the oxides of the less active metals are frequently reduced in a stream of hydrogen (*cf.* p. 244).

When the ore is a **carbonate**, it is first heated strongly to drive out the carbon dioxide (*cf.* p. 322): $FeCO_3 \rightleftarrows FeO + CO_2 \uparrow$, and then the oxide is treated according to one of the above mentioned methods. When the ore is a **sulphide**, it has to be roasted, or calcined (p. 256), in order to remove the sulphur, and the resulting oxide is then treated as described above.

Chlorides and **fluorides** of the metals can be decomposed by heating with metallic sodium. This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways, can be obtained easily by **electrolysis** of the fused chloride or of some other simple compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

Compounds of the Metals: Oxides and Hydroxides. — The **oxides** may be made by direct burning of the metal, by heating the nitrates (*cf.* p. 296), the carbonates (*cf.* p. 322), or the hydroxides: $Ca(OH)_2 \rightleftarrows CaO + H_2O \uparrow$. They are practically insoluble in water, although the oxides of the metals of the alkalies and of the metals of the alkaline earths interact with water rapidly to give the hydroxides. Oxides are usually stable. Those of gold, platinum, mercury, and silver decompose when heated, yet with increasing difficulty in this order. The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals (having the form K_2O), if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form MgO, when this is the only oxide which they furnish, are base-forming. Those of the trivalent metals of the form Al_2O_3, known as **sesquioxides** (Lat. *sesqui-*, one-half more), are the least basic of the basic oxides. The oxides of the forms SnO_2, Sb_2O_5, CrO_3, and Mn_2O_7, in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalies and alkaline earths, by direct union of water with the oxides. They are produced also by double decomposition when a soluble hydroxide acts upon a salt (*cf.* p. 239). All hydroxides, except those of the alkali metals, lose the elements of water when heated, and the oxide remains. In some cases the loss takes place by stages, just as was

the case with orthophosphoric acid (p. 309). Thus lead hydroxide $Pb(OH)_2$ (*q.v.*) first gives the hydroxide $Pb_2O(OH)_2$, then $Pb_3O_2(OH)_2$, and then the oxide PbO. The hydroxides, with the exception of those of the metals of the alkalies and alkaline earths, are all little soluble in water. The hydroxides of mercury and silver, if they are formed at all, are evidently unstable, for, when either material is dried, it is found to contain nothing but the corresponding oxide.

Compounds of the Metals: Salts. — It may be said, in general, that each metal may form a salt by combination with each one of the acid radicals. In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts. The salts are classified according to the acid radicals which they contain.

The **chlorides** may be made by the direct union of chlorine with the metal (*cf.* p. 113), or by the combined action of carbon and chlorine upon the oxide (*cf.* p. 344). The latter method is used in making chromium chloride. The general methods for making any salt (p. 123), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water. Silver chloride, mercurous chloride, and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without decomposition, but hydrolysis is conspicuous in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (*cf.* p. 353). The chlorides of some of the bivalent metals are hydrolyzed also, but, as a rule, only when they are heated with water. This is the case with the chlorides of magnesium, calcium, and zinc. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal, and so are preferred for the production of the spectrum (*q.v.*) of the metal, and for fixing the atomic weight of the metal by use of the vapor density. Some of the metals form two or more different chlorides. For example, indium gives InCl, $InCl_2$, and $InCl_3$.

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (*cf.* p. 254). In one or two cases they are made by the reduction of the sulphate with carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the hydroxides, and those of the metals of the alkaline earths are partially hydrolyzed (*cf.* p. 254).

The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (*cf.* p. 321). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are lithium carbide Li_2C_2, barium and strontium carbides BaC_2 and SrC_2, aluminium carbide Al_4C_3, manganese carbide MnC, and the carbides of potassium and glucinum. Others, such as those of molybdenum CMo_2 and chromium Cr_3C_2, are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. They are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic that these metals do not form stable carbonates (*cf.* pp. 347, 354).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 312). With the exception of the salts of sodium and potassium, all the salts of both these classes are insoluble.

For the **exact solubilities** of a large number of **bases and salts** at 18°, see the **Table inside the cover**, at the front of this book. **Solubilities at all temperatures** are shown in the **diagram**, Fig. 40, p. 104.

Exercises. — 1. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic?

2. What is meant by the same terms when applied to an hydroxide?

3. Compare the molar solubilities at 18°, (*a*) of the halides of silver, and (*b*) of the carbonates and (*c*) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

4. What is the molar concentration of chloride-ion in saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

CHAPTER XXXIII

THE METALLIC ELEMENTS OF THE ALKALIES: POTASSIUM AND AMMONIUM

THE metals of this family, with their atomic weights, are:

Lithium	7.0	Rubidium	85.5
Sodium	23.0	Caesium	132.9
Potassium	39.1		

The Chemical Relations of the Metallic Elements of the Alkalies. — The metals which are chemically most active are included in this group, and the activity increases with rising atomic weight, caesium being the most active positive element of all. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. All of these metals decompose water violently (*cf.* p. 66), liberating hydrogen. The hydroxides which are formed by this action are exceedingly active bases, that is to say, they give a relatively large concentration of hydroxide-ion in solutions of a given molecular concentration (p. 229). In the dry form these hydroxides are not decomposed by heating, while the hydroxides of all other metals lose water more or less easily. In all their compounds the metals of the alkalies are univalent.

The compounds of ammonium will be discussed in connection with those of potassium, to which they present the greatest resemblance.

The solubilities are often decisive factors in connection with the preparation and use of salts. The reader will find most of these in the table on the inside of the cover, at the front of this book, or in the diagram on p. 104, and, as a rule, the values will not be repeated in the descriptive paragraphs.

POTASSIUM.

Occurrence. — Silicates containing potassium, such as feldspar and mica (p. 348), are constant constituents of volcanic rocks. These minerals are not used commercially as sources of potassium

compounds. The salt deposits (see below) contain potassium chloride, alone (sylvite) and in combination with other salts, and most of the compounds of potassium are manufactured from this material. Part of our potassium nitrate, however, is purified Bengal saltpeter (p. 292). Potassium sulphate occurs also in the salt layers.

Preparation. — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. Globules of the metal appeared at the negative wire. Electrolytic processes have just come into use commercially, molten potassium chloride being the substance decomposed. Castner's reduction process involves the heating of potassium hydroxide with a spongy mass which is essentially a carbide of iron (CFe_2). The latter is made by heating together pitch and iron filings:

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K.$$

The potassium passes off as vapor, and is condensed.

Physical and Chemical Properties. — Potassium is a silver-white metal which melts at 62.5°. It boils at 667°, giving a green vapor.

The density of the vapor shows the molecular weight of potassium to be about 40, so that the vapor is a monatomic gas. The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of oxygen from the air to permit much oxidation of the potassium to take place. A white, crystalline **hydride** KH is formed when hydrogen is passed over potassium heated to 360°. When thrown into water it gives potassium hydroxide, and the hydrogen is liberated.

Potassium Chloride KCl. — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During the evaporation of such waters, however, the potassium compounds tend to accumulate in the mother-liquor while sodium chloride is being deposited. Hence the upper layers of salt deposits are the richest in compounds of potassium. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt. Above this are 25–30 meters of salt layers in which the potassium salts are chiefly found.

The chief forms in which potassium chloride is found in the salt beds are sylvite (KCl) and carnallite ($KCl,MgCl_2,6H_2O$). The latter salt is heated with a small amount of water, or with a mother-liquor obtained from a previous operation and containing sodium and magnesium chlorides. The magnesium sulphate which it contains as an impurity remains undissolved. From the clear liquid, when it cools, potassium chloride is deposited first and then carnallite. The former is taken out and purified, and the latter goes through the process again. This potassium chloride is the source from which most of our potassium hydroxide and potassium carbonate, as well as salts of minor commercial importance, are made. It is a white substance crystallizing in cubes, melting at about 750°, and slightly volatile at high temperatures.

The Other Halides of Potassium. — When iodine is heated in a strong solution of potassium hydroxide, potassium iodate and **potassium iodide** are both formed (p. 198):

$$6KOH + 3I_2 \rightarrow 5KI + KIO_3 + 3H_2O.$$

The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. Another method of preparation consists in rubbing together iodine and iron filings under water. The soluble ferrous iodide (FeI_2) thus formed is then treated with additional iodine and gives a substance Fe_3I_8, intermediate in composition between ferrous and ferric iodides. This is also soluble. When potassium carbonate is added to the solution, a hydrated magnetic oxide of iron is precipitated, carbon dioxide escapes, and evaporation of the filtered solution gives potassium iodide:

$$Fe_3I_8 + 4K_2CO_3 + 4H_2O \rightarrow 8KI + Fe_3(OH)_8 + 4CO_2.$$

The salt forms large, somewhat opaque cubes (m.-p. 623°). It is used in medicine and in photography (*q.v.*).

Potassium bromide KBr may be made in either of the ways used for the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates (*q.v.*).

The **fluoride of potassium** K_2F_2 may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent white salt. When treated with an equi-molecular quantity of hydrofluoric acid it forms **potassium-hydrogen fluoride** KHF_2, a white salt which is also very soluble.

Potassium Hydroxide KOH.— This compound, known also as **caustic potash**, and sometimes as potassium hydrate, was formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):

$$Ca(OH)_2(\text{solid}) \rightleftarrows Ca(OH)_2(\text{dslvd}) \rightleftarrows \left.\begin{matrix} 2OH' + Ca^{\cdot\cdot} \\ K_2CO_3 \rightleftarrows 2K^{\cdot} + CO_3'' \end{matrix}\right\} \rightleftarrows CaCO_3(\text{dslvd}) \rightleftarrows CaCO_3\ (\text{solid}).$$

The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases. On account of the very limited solubility of the calcium hydroxide (0.17 g. in 100 g. Aq), the water takes up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is, however, still more insoluble (0.0013 g. in 100 g. Aq) than is the hydroxide, and hence the action goes forward. After the precipitate has settled, the potassium hydroxide is obtained by evaporation of the clear liquid, $K^{\cdot} + OH' \rightarrow KOH$.

Recently much potassium hydroxide has been manufactured by

FIG. 62.

electrolytic processes. When a solution of potassium chloride is electrolyzed, chlorine is liberated at the anode, and hydrogen and potassium hydroxide at the cathode. These two sets of products must be kept apart, since by their interaction potassium hypochlorite and potassium chloride would be formed (*cf.* p. 189). In the Castner-Kellner apparatus (Fig. 62), which serves for making either potassium or sodium hydroxide, the two end compartments are filled with potassium chloride solution (or brine) and contain the graphite anodes. The central compartment contains potassium

forming an amalgam (p. 302). The layer of me
beneath the partitions, and a slight rocking motion gi
by the cam (*C*) causes the amalgam to flow below the
the central compartment. Here the sodium leaves t
the form of sodium ions and is attracted by the ca
this, hydrogen from the water is discharged, and
hydroxide-ion, together with the metal-ion, constitu
or sodium hydroxide:

$$2K^{\cdot} + 2H^{\cdot} + 2OH' + 2\ominus \rightarrow 2K^{\cdot} + 2OH' +$$

A slow influx of salt solution to the end compartments,
of the alkaline solution in the central cell, are mair
overflowing liquid contains 20 per cent of the alkali.
no undecomposed chloride present in the part of the s
contains the hydroxide, simple evaporation to dryness
solid alkali.

Potassium hydroxide is exceedingly soluble in wate
quently, instead of being crystallized from solution,
residue from evaporation is cast in sticks. The hydro
deliquescent. It also absorbs carbon dioxide from th
potassium carbonate. Solutions of the hydroxide hav
ingly corrosive action upon the flesh, decomposing it
mass by hydrolyzing the albuminous and other sub
solution, the base is highly ionized, furnishing a high c
of hydroxidion. Commercially it is chiefly employed ir

Potassium Chlorate $KClO_3$. — The preparation of this salt by interaction of potassium chloride with calcium chlorate, has already been described (p. 195). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials required. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the materials generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at about 351°, and at a temperature slightly above this the visible liberation of oxygen begins (*cf.* pp. 55, 196). On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component, along with antimony trisulphide, of the heads of Swedish matches. It is also used in medicine.

Potassium perchlorate $KClO_4$, formed by the heating of the chlorate (p. 196), gives white crystals belonging to the rhombic system.

The mode of preparing **potassium bromate** $KBrO_3$ and **potassium iodate** KIO_3 has already been described (pp. 197, 198). Potassium iodate may be made also very conveniently by melting together potassium chlorate and potassium iodide at a low temperature. The iodate is much less soluble (see Table) than the chloride, and the mixture may be separated by crystallization from water.

Potassium Nitrate KNO_3. — The formation of this salt in nature and its mode of extraction and purification have already been described (p. 292). This source of supply proved insufficient, for the first time, during the Crimean war (1852–55), and a method of manufacture from Chili saltpeter (sodium nitrate), which is a much cheaper substance, was introduced. Sodium nitrate and potassium chloride are heated with very little water, and the sodium chloride produced by the action, which is a reversible one, is by far the least soluble of the four salts (see Diagram, p. 104). On the other hand, at this temperature, the potassium nitrate is by far the most soluble. Hence the hot liquid drained from the crystals contains the required salt, and most of the sodium chloride is in the form of a precipitate. If the solubility curve of potassium nitrate (p. 104) is examined, it will be seen that this salt is but slightly soluble in cold water, and hence most of it is deposited when the solution cools. The crystals are mixed with little sodium chloride,

for, as the curve shows, common salt is little less soluble at 10° than it is at 100°.

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 63). It melts at about 340°, and when more strongly heated gives off oxygen, leaving potassium nitrite (p. 299). Although it does not form a hydrate the crystals inclose small portions of the mother-liquor, and consequently contain both water and impurities. When heated, the crystals fly to pieces explosively (**decrepitate**), on account of the vaporization of this water. Many substances which form large crystals and do not melt at a low temperature, behave in the same way and for the same reason. In consequence of this, the purest salt is made by violent stirring of the solution during the operation of crystallization, the result being the formation of a crystal-meal.

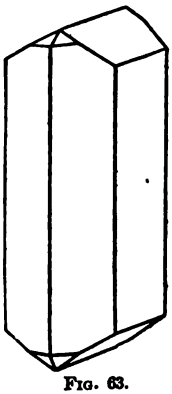


FIG. 63.

Potassium nitrate is used chiefly in the manufacture of **gunpowder**, which contains 75 per cent of the highly purified salt. The other components are 10 per cent of sulphur, 14 per cent of charcoal, and about 1 per cent of water. The ingredients are intimately mixed in the form of paste, and the material when dry is broken up and sifted, grains of different sizes being used for different purposes. The chemical action which takes place when gunpowder is fired in an open space gives chiefly potassium sulphide, carbon dioxide, and nitrogen:

$$2KNO_3 + 3C + S \rightarrow K_2S + 3CO_2 + N_2.$$

The explosion occurring in firearms follows a much more complex course, and half of the solid product is said to be potassium carbonate. The pressure, at the temperature of the explosion, if the gases could be confined within the volume originally occupied by the gunpowder, would reach about forty-four tons per square inch. In recent years common gunpowder has been displaced largely by **smokeless powder**, of which substances related to gun-cotton (pp. 294, 301) are the chief components.

Potassium Carbonate K_2CO_3.—This salt is manufactured from potassium chloride, from the Stassfurt deposits. The chloride is

heated with magnesium carbonate (magnesite), water, and carbon dioxide under pressure:

$$2KCl + 3MgCO_3 + CO_2 + 5H_2O \rightarrow 2KHMg(CO_3)_2,4H_2O + MgCl_2.$$

The hydrated mixed salt is separated from the liquid containing magnesium chloride and decomposed by heating with water at 120°. The product is a solution of potassium carbonate, from which the precipitated magnesium carbonate is removed by filtration. In some districts potassium carbonate is still extracted from wood-ashes.

This salt is usually sold in the form of an anhydrous powder (m.-p. over 1000°). When crystallized from water it gives a hydrate $2K_2CO_3,3H_2O$. It is deliquescent. Its aqueous solution, like that of sodium carbonate (*cf.* p. 353), has a marked alkaline reaction. The commercial name of the substance is **pearl ash**. It is used in making soft soap and hard glass. It is also employed, by interaction with acids, in making salts of potassium.

Potassium Cyanide KNC. — This salt is made by heating together dry potassium ferrocyanide (*q.v.*) and potassium carbonate. The ferrocyanide acts as if it were a mixture of potassium cyanide and ferrous cyanide: $K_4Fe(CN)_6 \rightarrow 4KCN + Fe(CN)_2$. The latter, by interaction with the potassium carbonate, would give potassium cyanide and ferrous carbonate, but this in turn, is decomposed by heat into ferrous oxide, which is insoluble, and carbon dioxide:

$$K_4Fe(CN)_6 + K_2CO_3 \rightarrow 6KCN + FeO + CO_2.$$

When the residue is extracted with water, only the potassium cyanide dissolves, and it is easily crystallized in pure form from the solution.

Potassium cyanide is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. The acid is so feeble as to be liberated both by the moisture and by the carbon dioxide of the air, and hence this salt always has an odor of hydrocyanic acid. Potassium cyanide is used in electroplating (*q.v.*), and in extracting gold (*q.v.*) from its ores.

The preparation of **potassium cyanate** KCNO, a white, easily soluble salt, and of **potassium thiocyanate** KCNS, a white, deliquescent salt, have already been described (p. 336).

The Sulphate and Bisulphate. — Potassium sulphate K_2SO_4 is a constituent of several double salts found in the Stassfurt deposits. It is extracted from **schoenite** $MgSO_4.K_2SO_4.6H_2O$ and **kainite** $MgSO_4.MgCl_2.K_2SO_4.6H_2O$. The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no water of crystallization and melt at 1,066°. This salt is employed in preparing alum (q.v.) and is much used as a **fertilizer**. Since plants take up solutions through their cell walls, they can absorb soluble compounds only. They are, therefore, dependent, for the potassium compounds which they require, upon the weathering out of soluble potassium compounds from insoluble silicates containing potassium (p. 345) found in the soil. The weathering takes place too slowly to furnish a sufficient supply for many crops, particularly that of the sugar-beet. Hence potassium sulphate is mixed directly with the soil.

Potassium-hydrogen sulphate (bisulphate) $KHSO_4$ is made by the action of sulphuric acid upon potassium sulphate: $K_2SO_4 + H_2SO_4 = 2KHSO_4$. It crystallizes from water, in which it is very soluble, in tabular crystals. Its properties are similar to those of sodium bisulphate which have already been described (p. 265).

Sulphides of Potassium. — By the treatment of a solution of potassium hydroxide with excess of hydrogen sulphide, a solution of **potassium-hydrogen sulphide** is obtained. Evaporation of the solution gives a deliquescent, solid hydrate $2KHS,H_2O$. When the solution, before evaporation, is treated with an equivalent amount of potassium hydroxide, and the water is driven off, the **sulphide** K_2S remains behind (*cf.* p. 253):

$$KHS + KOH \rightleftarrows K_2S + H_2O.$$

Considerable amounts of sulphur can be dissolved in solutions of either of these sulphides. By evaporation of the resulting yellow liquids, various **polysulphides** have been obtained. To some of these have been ascribed the formulæ K_2S_3, K_2S_4, and K_2S_5 (*cf.* p. 255). Similar substances are produced, as a result of the liberation and

ombination of sulphur, when the solutions are exposed to the idizing action of the air:

$$2KHS + O_2 \rightarrow 2KOH + 2S.$$

Properties of Potassium-ion $K^{\cdot}$: Analytical Reactions.—The ositive ionic material of the potassium salts is a colorless substance. unites with all negative ions, and most of the resulting compounds e fairly soluble. For its recognition we add solutions containing ose ions which give with it the least soluble salts. Thus, with hloroplatinic acid H_2PtCl_6 it gives a yellow precipitate of potassium hloroplatinate K_2PtCl_6. Since nearly one part of this salt dissolves n 100 parts of water, the test is far from being a delicate one. Picric cid (p. 294) gives potassium picrate $KC_6H_2(NO_2)_3O$, which is much ess soluble in water (0.4 parts in 100 at 15°). Perchloric acid and hydrofluosilicic acid likewise give somewhat insoluble salts of potassium. **Potassium-hydrogen tartrate** $KHC_4H_4O_6$ is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The neutral tartrate $K_2C_4H_4O_6$ is much more soluble. The latter may be obtained by treating the precipitate with a solution of potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

A much more delicate test for the recognition of a potassium compound consists in the examination by means of the spectroscope of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is recognizable by the eye.

Rubidium and Caesium. — In 1860 Bunsen discovered several new lines in the spectrum given by materials derived from the salts in Dürkheim mineral water. Two new elements of the alkali group were found to cause their presence, and were named, from the colors of the lines which they gave, rubidium (red) and caesium (blue). Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

The metals may be obtained by heating their hydroxides with magnesium powder. The hydroxides of these two elements are more active than potassium hydroxide. Their salts are very much like those of potassium.

AMMONIUM

The compounds of ammonium [illegible] a place with those of the alkali metals [illegible] in aqueous solution they give ammonium-[illegible] NH_4, a substance which in its behavior closely resembles potassium. [illegible] of the special properties peculiar to ammonium compounds and particularly the properties of ammonium hydroxide NH_4OH have been discussed in detail already (pp. [illegible]).

Salts of Ammonium. — **Ammonium chloride** NH_4Cl known commercially as **sal-ammoniac**. Like all the other compounds of ammonium is prepared from the ammonia dissolved by the water used to [illegible] illuminating-gas (p. [illegible]). It is purified by sublimation, and [illegible] forms a compact fibrous mass. When heated to 350° it volatilizes and is almost completely dissociated into ammonia and hydrogen chloride at this temperature (p. [illegible]).

Ammonium nitrate NH_4NO_3 is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid. When heated gently it decomposes, giving nitrous oxide and water (p. [illegible]). It is used as an ingredient in fireworks and explosives.

When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate** NH_4HCO_3. This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the **neutral carbonate** $NH_4{}_2CO_3$ is formed. But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

Ammonium thiocyanate NH_4NCS (*cf.* p. 179) is a white salt which finds some application in analysis.

Ammonium sulphate $(NH_4)_2SO_4$ is a white salt which is used chiefly as a fertilizer. By electrolysis of a concentrated solution of the **bisulphate** NH_4HSO_4, ammonium **persulphate** $(NH_4)_2S_2O_8$, which is less soluble, is formed and crystallizes out (*cf.* p. 267).

Solutions of **ammonium-hydrogen sulphide** NH_4HS and **ammonium sulphide**, $(NH_4)_2S$, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water into the acid sulphide a

ammonium hydroxide, its behavior being like that of sodium sulphide (p. 253):

$$2\,NH_3 + H_2S \rightleftarrows (NH_4)_2S \leftrightarrows \left.\begin{array}{r} 2\,NH_4^{\cdot} + S'' \\ H_2O \leftrightarrows \quad OH' + H^{\cdot} \end{array}\right\} \leftrightarrows HS'.$$

It is used for the precipitation of sulphides, such as zinc sulphide, which are insoluble in water. Although the S″ ions are not numerous at any moment, disturbance of the equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply. The liquid smells strongly of ammonia and hydrogen sulphide, on account of the dissociation of the parent molecules by reversal of the above equilibria.

The solutions, when pure, are colorless. They dissolve free sulphur, giving yellow **polysulphides** similar to those of potassium (p. 368). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

Ammonium Amalgam. — When a salt of ammonium is decomposed by electrolysis the $NH_4^{\cdot}$, upon its discharge, ordinarily gives ammonia and hydrogen, and no substance NH_4 is obtained. If, however, a pool of mercury is used as the negative electrode, the NH_4 forms an amalgam with it, and there seems to be no doubt that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of the substance is only temporary. The same material may be obtained by putting sodium amalgam into a strong solution of a salt of ammonium. The action is a displacement of one ion by another (p. 243):

$$Na(\text{dslvd in mercury}) + NH_4^{\cdot} \rightarrow NH_4(\text{dslvd in mercury}) + Na^{\cdot}.$$

This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances other than metals are not miscible with mercury.

Ammonium-ion $NH_4^{\cdot}$: Analytical Reactions. — Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate $(NH_4)_2PtCl_6$, and to a less extent ammonium-hydro-

gen tartrate $NH_4HC_4H_4O_6$, are insoluble compounds, and their pre-cipitation is used as a test. The surest means of recognising ammo-nium compounds, however, consists in adding a soluble base to the substance (*cf.* p. 283). The ammonium hydroxide, which is thus formed, gives off ammonia, and the latter may be detected by its odor.

Exercises. — 1. What kind of metals will, in general, interact with solutions of bases (*cf.* p. 356)?

2. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

3. How should you set about making, (*a*) a borate of potassium, (*b*) potassium pyrophosphate, (*c*) ammonium nitrite, (*d*) ammonium chlorate, (*e*) ammonium iodide?

CHAPTER XXXIV

SODIUM AND LITHIUM. IONIC EQUILIBRIUM CONSIDERED QUANTITATIVELY

SODIUM chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain sodium salts of organic acids, just as land-plants contain potassium salts. Chili saltpeter, cryolite, and albite (a soda feldspar) are important minerals.

Preparation. — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is manufactured by Castner's process, which is used also for potassium (p. 361), and by the electrolysis of fused sodium hydroxide by a method likewise invented by Castner. In the latter case the negative electrode projects through the bottom of the iron vessel containing the fused hydroxide. This electrode is surrounded by a wire-gauze partition, which is surmounted by a bell-shaped vessel of iron. The positive electrode is an iron cylinder surrounding the gauze. The sodium and hydrogen liberated at the cathode, being lighter than the fused mass, ascend into the iron vessel, under the edge of which the hydrogen escapes. Oxygen is set free at the anode.

Properties. — Sodium is a soft, shining metal, melting at 95.6° and boiling at 742°. The vapor is a monatomic gas. The general chemical properties have already been given (p. 360). The metal unites with hydrogen to form a **hydride** NaH, which resembles potassium hydride (p. 361). The **amalgam** with mercury when it contains more than a small amount of sodium, is solid, and probably contains one or more compounds of the two elements. This amalgam is often used instead of the metal sodium, since the dilution or combination with mercury makes the interactions of the metal more easily controllable. Sodium is used in the manufacture of many complex carbon compounds which are employed as drugs and dyes.

Sodium Chloride NaCl. — Common salt is obtained from the salt deposits of Stassfurt, Reichenhall (near Salzburg), in Cheshire, at Syracuse and Warsaw in New York, at Salina in Kansas, in Utah, California, and many other districts. Natural brines are obtained from wells in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water. Natural brines, which are sometimes dilute, are often concentrated by dripping over extensive ricks composed of twigs. When the resulting brine is allowed to evaporate slowly by the help of the sun's heat, large crystals, sold as "solar salt," are obtained. By the use of artificial heat and stirring smaller crystals of greater purity can be secured. Salt intended for table use must be freed from the traces of magnesium chloride (q.v.) present in the original brine or deposit, for this impurity causes it to absorb moisture more vigorously from the air. The purest salt for chemical purposes is precipitated from a saturated solution of salt by leading into it hydrogen chloride gas. Explanation of this effect will be given presently (see pp. 385–387).

Common salt crystallizes in cubes, the faces of which are usually hollow. The crystals decrepitate (p. 366) when heated, and melt at about 820°. Common salt is the source of all sodium compounds, with the exception of the nitrate. From it come also most of the chlorine and hydrogen chloride used in commerce.

The Hydroxide and Oxides. — **Sodium hydroxide** NaOH, called also, colloquially, **caustic soda**, is prepared by the action of slaked lime upon sodium carbonate, and by the electrolysis of a solution of sodium chloride, in both cases precisely as is potassium hydroxide (p. 363). Sodium hydroxide is a highly deliquescent substance. Its general chemical properties are identical with those of potassium hydroxide. It is used in the manufacture of soap, in the preparation of paper pulp, and in many other chemical industries.

Sodium peroxide Na_2O_2 is made by heating sodium at 300–400° in air which has been freed from carbon dioxide. This oxide is the sodium salt of hydrogen peroxide. When thrown into water it decomposes in part, in consequence of the heat developed, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved. By interaction with acids it yields hydrogen peroxide (p. 211). Sodium peroxide is now used com-

mercially for oxidizing and bleaching. The ordinary **sodium oxide** Na_2O is made in the same way as is potassium oxide (p. 364).

The Nitrate and Nitrite. — The occurrence and purification of **sodium nitrate** $NaNO_3$ have already been described (p. 292). Its crystals are of rhombohedral form (Fig. 9, p. 9). This salt is one of the best of fertilizers, since it furnishes to plants the nitrogen which they require in a very easily absorbed form. It is used also in the manufacture of potassium nitrate, and of nitric acid.

Sodium nitrite $NaNO_2$ is formed by heating sodium nitrate with metallic lead and recrystallizing the product (p. 299).

Manufacture of Sodium Carbonate. — Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's

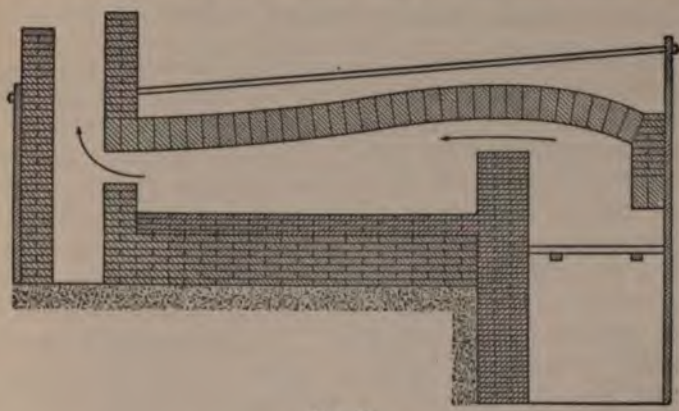


FIG. 64.

Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$, being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of sea-weed. The substance is manufactured from sodium chloride in two ways, namely by the Le Blanc process and by the Solvay process.

The **Le Blanc process** (1791) involves three chemical actions. In the first place, sodium chloride is treated with an equivalent amount of sulphuric acid in a large cast-iron or earthenware pan. The

containing running water in which it is absorbed. T
third actions which follow are conducted in one ope
consist in the reduction of the sodium sulphate by mea
coal and the interaction of the resulting sulphide o
chalk or powdered limestone:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2,$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$

In the less modern factories the salt-cake, limestone
stirred upon the hearth of a reverberatory furnace a
hand. The material is finally collected into balls, and
action is recognized by the fact that bubbles of carb
begin to force their way to the surface and cause littl
flame. The gas is produced by the action of the c
calcium carbonate, excess of both of these substances b
$CaCO_3 + C \rightarrow CaO + 2CO$. The production of this
porous texture to the material, which facilitates the s
sodium carbonate in the final stage. The porous pro
black-ash. In modern factories hand labor is saved b
black-ash furnace the form of a rotating cylinder, i
jections from the walls assist in bringing about comple
the materials during the action.

The black-ash varies very much in composition. I
contains 45 per cent of sodium carbonate, 30 per cen
sulphide, 10 per cent of calcium oxide, and a number of

black-ash by a systematic treatment of the ash with water. The ash is placed in a series of vessels at different levels, and a stream of water (30–40°) flows from one vessel to another, until, when it issues from the last, it is completely saturated with sodium carbonate. When the material in the first of the vessels has been exhausted, the water is allowed to enter the second vessel directly, and a vessel containing fresh black-ash is added at the lower end of the series. In this way the most nearly exhausted ash comes in contact with pure water, which is in the best position to dissolve the remaining sodium carbonate rapidly, while the fresh black-ash encounters a solution already almost at the point of saturation.

The saturated solution is evaporated in shallow pans placed on the flues of the furnaces, and the monohydrate Na_2CO_3,H_2O, which crystallizes from the hot liquid, is raked out and dried by heat, leaving **calcined soda.** When this material is recrystallized from water and is allowed to deposit itself from the solution at the ordinary temperature, the decahydrate $Na_2CO_3,10H_2O$, **soda crystals** or **washing soda,** appears.

The solid residue from the extraction of the black-ash is known as **tank waste,** and contains 35–55 per cent of calcium sulphide. This material contains the sulphur of the original sulphuric acid, and its treatment involves a problem of some difficulty. If it is dumped near the factory the sulphur is lost, and by slow weathering yellow solutions containing polysulphides flow from the decomposing heap into the streams, and offensive odors of hydrogen sulphide fill the air. The most effective process for the recovery of the sulphur and consequent abatement of this nuisance is that of Chance. The product is arranged in a series of cylinders through which is passed carbon dioxide from a kiln of special form. The hydrogen sulphide liberated in the first cylinder forms the acid sulphide with the material contained in the second:

$$2CaS + CO_2 + H_2O \rightarrow Ca(SH)_2 + CaCO_3.$$

The further action of the carbon dioxide on this product gives, finally, a mixture of gases containing a larger proportion of hydrogen sulphide. By burning this mixture with a limited supply of air, the sulphur is then secured in free condition:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

About 70,000 tons of sulphur are thus recovered annually.

Sodium tetraborate $Na_2B_4O_7,10H_2O$ (**borax**) form parent prisms. When heated it loses water, and l fusible anhydrous salt in glassy form. Its source been discussed under borates (p. 350). It is used in glazes for porcelain, in soldering, for bead reactio for preserving food.

Sodium metasilicate Na_2SiO_3 (*cf.* p. 346) is used wood and other materials, and for preserving egg is moistened with it and pressed in molds, forms, serviceable artificial stone.

Properties of Sodium-ion: Analytical Reactio ion $Na^{\cdot}$ is a colorless ionic material which unites wi ions. Practically all the salts so formed are soluble only ones which can be precipitated are sodium fluos made by the addition of hydrofluosilicic acid to a str a sodium salt, and sodium-hydrogen pyroantimoniat made by similar addition of the corresponding potass compounds of sodium confer a yellow color on the but this test is so delicate that it is shown by the tr contained in almost all substances.

Lithium.—Lithium occurs in lepidolite (a lithia mi gonite, and in other rare minerals. Traces of comp element are found widely diffused in the soil, and are

The metal behaves towards water and oxygen like sodium (p. 66). It unites directly and vigorously with hydrogen (LiH), nitrogen (Li_3N), and oxygen (Li_2O), forming stable compounds. The relative insolubility (see Table) of the hydroxide (LiOH), the carbonate (Li_2CO_3), and the phosphate ($Li_3PO_4,2H_2O$), is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame. A bright-red and a somewhat less bright orange line are seen in the spectrum. The carbonate is used in medicine.

Ionic Equilibrium, Considered Quantitatively.

In view of the predominance of ionic actions in the chemistry of the metals, and of the determinative effect of ionic equilibria on many actions, it is essential that we should be prepared in future for a more exact consideration of these phenomena than we have hitherto attempted. The whole basis for this exact consideration has already been supplied, and only more specific application of the principles is demanded. The basis referred to, which should now be studied as a preliminary to what follows, is contained in, (1) the discussion of chemical equilibrium in general (pp. 174–185), (2) the application of the same principles to ionic equilibrium (p. 224), and (3) the illustration of this application in the case of cupric bromide (pp. 233–236).

Excess of One Ion. — In the case of cupric bromide, we showed that increasing the concentration of the bromide ions displaced the equilibrium by favoring the union of the ions to form molecular cupric bromide: $2Br' + Cu^{\cdot\cdot} \rightarrow CuBr_2$. This we speak of as a **repression of the ionization** of the cupric bromide. Now, if the substance is a slightly ionized one, like a weak acid or a weak base, the repression of the ionization through the formation of molecules in this way may remove so many of that one of the ions which is not present in excess (corresponding to the $Cu^{\cdot\cdot}$ in the foregoing illustration), that the mixture will no longer respond to tests for the ion so removed. This is an interesting and very common case. The behavior of acetic acid, a weak, slightly ionized acid, will serve as an illustration.

In normal solution (60 g. in 1 l.) acetic acid is only .004 ioni (p. 228), so that, in the equation for the equilibrium,

$$(.996)\ HC_2H_3O_2 \rightleftarrows H^{\cdot}\ (.004) + C_2H_3O_2'\ (.004),$$

the relative proportions are as shown by the numbers in parenthes If the whole of the acid (60 g.) were ionized, there would be 1 g. hydrogen-ion per liter. Yet, even in this much smaller conc tration (.004 g. per liter), the acid taste of the $H^{\cdot}$ and its effect upo indicators can be distinctly recognized. If, now, solid sodi acetate is dissolved in the solution, the liquid *no longer gives an ac reaction* with one of the less delicate indicators, like methyl orang (*q.v.*). The explanation is simple. Sodium acetate is hig ionized. It gives, therefore, a large concentration of acetate-ion a liquid formerly containing very little. This causes a great increased union of the $H^{\cdot}$ ions and $C_2H_3O_2'$ ions and the forme being already very few in number, disappear almost entirel Hence the solution becomes, to all intents and purposes, neutr There is no less *acetic acid* present than before, but the concentratio of hydrogen-ion is very much smaller.

Formulation and Quantitative Treatment of the Case Excess of One Ion. — If the semi-mathematical mode of form lating an equilibrium (p. 180), as applied to the case of an ionog (p. 224), be employed here, the foregoing general statements may made more precise and the conclusions clearer. If $[H^{\cdot}]$ and $[C_2H_3O$ represent the molecular concentrations of hydrogen-ion and acetat ion, respectively, and $[HC_2H_3O_2]$ that of the acetic acid molecules equilibrium, then:

$$\frac{[H^{\cdot}] \times [C_2H_3O_2']}{[HC_2H_3O_2]} = K.$$

The value of K is constant, whether the strength of the solution acetic acid is great or small, and even when another substance wi a common ion is present. In the latter case, $[C_2H_3O_2']$ and [stand for the whole concentrations of each of these ionic substan from both sources.

Now, in normal acetic acid $[H^{\cdot}] = .004$, $[C_2H_3O_2'] = .004$ (for t number of each kind of ions is the same), and $[HC_2H_3O_2] = .9$ practically 1. Substituting in the formula:

$$\frac{0.004 \times 0.004}{1} = K\ (= 0.0_{4}16).$$

When sodium acetate is dissolved in the liquid until the solution is normal in respect to this substance also, the following additional equilibrium has to be considered:

$$(.47)\ NaC_2H_3O_2 \rightleftarrows Na^{\cdot}\ (.53) + C_2H_3O_2'\ (.53).$$

The concentration of acetate-ion from this source is .53, so that, in the mixture of acid and salt, the concentration of acetate-ion $[C_2H_3O_2']$ will be .53 + .004 = .534, or nearly 134 times larger than in the acid alone. Hence, in order that the product $[H^{\cdot}] \times [C_2H_3O_2']$ may recover, as it must, a value much nearer to the old one, $[H^{\cdot}]$ must be diminished to something like $\frac{1}{134}$ of its former magnitude. That is, $[H^{\cdot}]$ will become equal to about 0.00003, the rest of the hydrogen-ion uniting with a corresponding amount of the acetate-ion to form molecular acetic acid. The effect of adding this amount of sodium acetate therefore is, as we have seen, to reduce the concentration of the *hydrogen-ion* below the amount which can be detected by use of an indicator like methyl-orange.

This effect is of course reciprocal, and the ionization of the sodium acetate will be reduced also. But the acetate-ion furnished by the acetic acid is relatively so small in amount (.00003 against .53) that the effect it produces on the ionization of the salt is imperceptible.

It will be noted that the acetate-ion and hydrogen-ion disappear in equivalent quantities, for they unite. There is, however, so much of the former that its loss goes unremarked, while there is so little of the latter that almost none of it remains. When substances of more nearly equal degrees of ionization are used, *both effects are equally inconspicuous.* Thus, sodium chloride and hydrogen chloride in normal solutions yield approximately equal concentrations of chloride-ion (.784 and .676). Hence, if one mole of sodium chloride were to be dissolved in the portion of water already containing one mole of hydrogen chloride, the concentration of the chloride-ion, at a very rough estimate, would be nearly doubled. If this doubling of the concentration of chloride-ion almost halved that of the hydrogen-ion (.784), in order that the expression $[Cl'] \times [H'] \div [HCl]$ might remain constant, the concentration of the hydrogen-ion would still be about .400 and therefore 100 times as great as in molar acetic acid. It is thus altogether impossible to reduce the concentration of the hydrogen-ion given by an *active* acid like hydrochloric acid below the limit at which indicators are affected, for there is no way

of introducing the enormous concentration of the other ion [illegible] the theory demands.

With more crude means of observation than indicators [illegible] effects like this last may sometimes be rendered visible. This [illegible] the case with cupric bromide solution, to which potassium [illegible] was added (p. 235). The blue of the cupric-ion disappeared [illegible] view, while much cupric-ion was still present, because the [illegible] color of the molecular cupric bromide covered it up completely.

Special Case of Saturated Solutions. — The commonest [illegible] well as the most interesting application of the conceptions devel[illegible] above is met with in connection with saturated solutions, especi[illegible] those of relatively insoluble substances.

The situation in a system consisting of the saturated solution [illegible] excess of the solute has been discussed already (p. 102). In the [illegible] of potassium chlorate, for example, we have the following scheme [illegible] equilibria.

$$KClO_3 \text{ (solid)} \rightleftarrows KClO_3 \text{ (dslvd)} \rightleftarrows K^{\cdot} + ClO_3'.$$

Solution of the solid is promoted by the solution pressure of the mole[illegible]cules, while it is opposed by the osmotic pressure of the dissolve[illegible] substance and the solution is saturated when these tendencies produce equal effects (p. 103). Now it must be noted that [illegible] tendency directly opposed to the solution pressure is the par[illegible] osmotic pressure of the dissolved *molecules* alone. The chief co[illegible]tents of the solution, the molecules and two kinds of ions of the sa[illegible] and any foreign material that may be present, are like a mixture [illegible] gases, and the principle of partial pressure (p. 60) is to be applie[illegible] The ions and the foreign material do not deposit themselves upon the solid, and take, therefore, no part *directly* in the equilibrium which controls solubility. In respect to this the ions are themselves foreign substances. Hence the conclusion may be stated that, in **solutions saturated at a given temperature by a given solute, the concentration of the dissolved molecules of the solute considered by themselves will be constant whatever other substances may be present.**

The total solubility of a substance, as we have used the term hitherto, is made up of a molecular and an ionic part. The latter, as we shall presently see, is not constant when a foreign substance containing a common ion is already in the liquid. Since the treat-

nt of the subject requires us now to distinguish between the two tions of the solute, a diagram (Fig. 65) will assist in emphasizing distinction. The material at the bottom is the salt. The lecules and ions are to be thought of as being mixed and as being esent in numbers represented by the factors n and m. Since no reign body is present, the two ions in this case are equal in number. When we now apply these ideas to the mathematical expression the relation:

$$\frac{[K^{\cdot}] \times [ClO_3']}{[KClO_3]}$$

e perceive that, in a saturated solution, $[KClO_3]$, the concentration the molecules, is *constant*. Transposing, we have

$$[K^{\cdot}] \times [ClO_3'] = K\,[KClO_3'] = K'.$$

Hence the relation leads to the important conclusion that, **in a saturated solution the product of the molar concentrations of the ions is constant.*** This product is called the **ion-product constant** for the substance. The law of the constancy of the ion-product in a saturated solution s one of the most useful of the principles of chemistry. It enables us to explain all the varied phenomena of precipitation and of the solution of precipitates in a consistent manner. These applications of the principle will be explained in the next chapter. One curious kind of precipitation will be described here, however, as an illustration of the use of the principle.

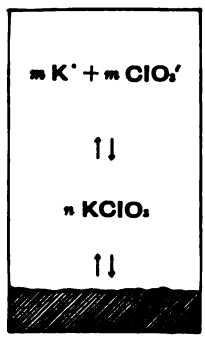


FIG. 65.

Illustration of the Principle of Ion-Product Constancy. — When, to a *saturated* solution of one of the less soluble salts, a strong solution of a salt having *one ion in common* with the first salt is added, precipitation of the first salt frequently takes place. This happens, for example, with a

* The principle of constant concentration of dissolved molecules, stated above, has been shown to express the facts very inaccurately. Now the principle of the constancy of the ratio of the ion-product to the concentration of the molecules is also inaccurate, yet in such a way that the two errors neutralize one another. Thus, the principle of ion-product constancy here given is in itself fairly exact.

[illegible]

[illegible] ... minimity product ... [illegible] ... The little part of any [illegible] ... made up of the smaller of the two concentrations ... [illegible] ... plus an equivalent amount ... of the concentration of the other ion. The rest of th[illegible] ionic substance is part of the solubility of some other comp[illegible]

Other Illustrations. — The precipitation of sodium c[illegible] from a saturated solution, by the introduction of gaseous hy[illegible] chloride (p. 374), is to be explained in the same manner[illegible] equilibria:

$$NaCl \text{ (solid)} \rightleftarrows NaCl \text{ (dslvd)} \rightleftarrows Na^{\cdot} + Cl'$$

reversed by the introduction of additional Cl′ from the very able, and highly ionized HCl.

The evolution of a steady stream of hydrogen chloride is often omplished by allowing concentrated sulphuric acid to flow into urated hydrochloric acid:

$$H^{\cdot} + Cl' \rightleftarrows HCl\ (dslvd) \rightleftarrows HCl\ (gas).$$

e effect is due in part to repression of the ionization of the hydro- n chloride and elimination of molecules of the gas from the water hich is already saturated with molecules of the same kind. The salting out" of soap (p. 335) is probably a similar phenomenon.

Exercises. — 1. The vapor density of sodium peroxide has not een determined. Why is the formula Na_2O_2 assigned to it?

2. Construct a scheme of equilibria (p. 253) showing the hydroly- is of calcium sulphide. Why does the presence of calcium hydroxide iminish the tendency to hydrolysis?

3. Show the application of the principle of ion-product constancy o the salting out of soap (p. 335).

4. What will be the effect of adding a concentrated solution of lver nitrate to a saturated solution of silver sulphate (see Table of olubilities)?

CHAPTER XXXV

THE METALLIC ELEMENTS OF THE ALKALINE EARTHS

The Chemical Relations of the Elements. — The me of this group, **calcium** (Ca, at. wt. 40.1), **strontium** (Sr, at. wt. 87 and **barium** (Ba, at. wt. 137.4), constitute a typical chemical fam both in the qualitative resemblance to one another of the elem and of the corresponding compounds, and in the quantitative va tion in the properties with increasing atomic weight. The me themselves displace hydrogen vigorously from cold water, gi hydroxides. The solutions of these hydroxides, although dis on account of a rather small solubility, are strongly alkaline reaction. The high degree of ionization of the hydroxides rea the hydroxides of the metals of the alkalies, and their relat insolubility the hydroxides of the "earths" (*q.v.*).

In all their compounds, calcium, strontium, and barium are bi lent. The hydroxides are formed by union of the oxides with wa and are progressively less easy to decompose by heating, barium droxide being the hardest. The carbonates, when heated, yield oxide of the metal and carbon dioxide, barium carbonate being most difficult to decompose. The nitrates, when heated moderat give the nitrites, but the latter are broken up by further hea and yield the oxide of the metal, and nitrogen tetroxide. these and other respects the compounds of the metals of the alk earths resemble those of the heavy metals and differ from tho the metals of the alkalies. Barium approaches the latter r nearly.

The table of solubilities (*q.v.*) shows that the chlorides and nitr of calcium, strontium, and barium are all soluble in water. solubility diminishing in the order given. The sulphates hydroxides cover a wide range from slight solubility to extr insolubility. Of the sulphates, 2100, 110, and 2.3 parts, respecti dissolve in one million parts of water. In the case of the hydro the order of magnitude is reversed, and the corresponding num

200, 630, and 2200. The carbonates are almost as insoluble as barium sulphate. The new element, radium (Ra, at. wt. 226.5), appears to belong to this family (see under Uranium).

Calcium Ca.

Occurrence. — The fluoride, and the various forms of the carbonate, sulphate, and phosphate which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. The element is found also in plants, and its compounds are constituents of the bones and shells of animals.

The Metal. — Calcium is made by electrolysis of the molten chloride. A hollow cylinder made of blocks of carbon bolted together and open above, forms the anode. A rod of copper hanging so that its end dips into the melt forms the cathode. The melting of the anhydrous calcium chloride with which the cylinder is filled is started by means of a thin rod of carbon laid across from the anode to the cathode. When the heat generated by the passage of the current through this highly resisting medium has melted a sufficient amount of the salt, the rod is removed, and the resistance of the fused material suffices to maintain the temperature. The calcium rises round the cathode and collects on the surface of the bath. By slowly elevating the copper cathode, the calcium, which adheres to it, may be drawn out of the fused mass in the form of a gradually lengthening, irregular rod. The rod of calcium is kept constantly in contact with the metal which accumulates on the surface, and thus forms one of the electrodes.

Calcium is a silver-white, crystalline metal (m.-p. 760°, sp. gr. 1.85) which is a little harder than lead, and can be cut, drawn, and rolled. It interacts rapidly with water. When dry and cold it is inactive, but when heated it unites vigorously with hydrogen, oxygen, the halogens, and nitrogen. On this account it is used in producing a high degree of evacuation. It burns in the air, giving a mixture of the oxide and nitride Ca_3N_2. The presence of the latter may be shown by the liberation of ammonia when water is added to the residue:

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3.$$

several industrial operations. Thus, it arises in tl ammonia from ammonium chloride by the action manufacture of potassium chlorate (p. 195), and in t process (p. 378). By evaporation of any solution, $CaCl_2,6H_2O$ is obtained in large, deliquescent, six-sid account of the great concentration of a saturated compound, the solid and solution do not reach a co librium with ice (*cf.* p. 204) until the temperature $-48°$. The hydrate, when mixed with ice, gives, tl efficient freezing mixture.

Calcium chloride, dehydrated by heating ($CaCl_2$), mass which is used in chemical laboratories for dr liquids.

Calcium chloride forms compounds, not only with with ammonia ($CaCl_2,8NH_3$) and with alcohol. Fo substances, therefore, quicklime is employed.

Calcium Fluoride CaF_2. — This compound occu fluorite or fluor-spar CaF_2. It crystallizes in cubes, water, and when pure is colorless. Natural specimen a green tint or show a violet fluorescence. It is forme tate when a soluble fluoride is added to a solution of a s

Fluorite is used in the etching of glass, as the source gen fluoride (p. 171). It is easily fusible, as its name i *fluere*, to flow), and is employed in metallurgical or

e variety, while marble is a distinctly crystalline form. Chalk * a deposit consisting of the calcareous parts of minute organisms. gg-shells, oyster-shells, coral, and pearls are other varieties of ganic origin.† Calcite and Iceland spar (Ger. *spalten*, to split) e pure crystallized calcium carbonate. The former occurs in flat ombohedrons, or in pointed, six-sided crystals (Fig. 33, p. 94) nown as scalenohedrons (" dog-tooth " spar) belonging to the same ystem.

When heated, calcium carbonate dissociates, giving carbon dioxide nd quicklime:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At ordinary temperatures the decomposition is imperceptible. On he contrary, atmospheric carbon dioxide, in spite of its very low partial pressure, combines with quicklime, giving " air-slaked " lime. As the temperature rises, however, **the tension of carbon dioxide** coming from the carbonate increases, and **has a fixed value for each temperature.** If it is continually allowed to escape, so that the maximum pressure is not reached, the whole of the salt eventually decomposes. At 812° the pressure reaches one atmosphere, and at 865° two atmospheres. The phenomenon is precisely similar to the dissociation of barium dioxide (*cf.* Brin's process, pp. 46, 184) and to the evaporation of a liquid (pp. 78–79).

Limestone is used in the manufacture of quicklime (*q.v.*) and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate ($CaSiO_3$). Large amounts also find application as building-stone.

Hard Water.— Calcium carbonate is almost insoluble in water. In the cold the solubility is a little over 1 part in 100,000; in hot water the solubility is even smaller. Water containing carbonic acid dissolves it more freely, on account of the formation of the more soluble calcium bicarbonate (*cf.* p. 324):

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$

At 15° a liter of water saturated with carbon dioxide (at 760 mm. pressure) dissolves 0.385 g. of the carbonate, whereas a liter of pure

* Blackboard "crayon" is usually made of gypsum and not of chalk.

† The hard coverings of crustacea and insects are not made of this substance, but of an organic material called chitin.

manent hardness " (for the action on soap, see p

The temporary hardness may be removed by a quantity of slaked lime sufficient to convert t acid into calcium carbonate. The permanen destroyed by the addition of sodium carbonate precipitated carbonate is allowed to settle or is tion.

When evaporated in steam-boilers hard wa heavy deposit of boiler-crust containing all th solution. Subterranean water, rich in carbon way to the roofs of caverns, loses its gas and giv The drippings form stalagmites on the floors.

Calcium Oxide and Hydroxide. — Pure o (**quicklime**) may be made by ignition of pure mar commercial purposes limestone is converted into In the United States the " long-flame " process, first charged with limestone and a fire is then left at the bottom, is the one most commonly used stone and coal are simply thrown, in alternate laye the products are withdrawn at the bottom. The flame " method, demands less fuel, since the oper and the structure is never allowed to cool, bu mixed with the ash of the coal. In many cases tion is removed by placing the fuel in cavities kiln.

ures mechanically, and then unites chemically to form **calcium hydroxide** $(CaOH)_2$:

$$CaO + H_2O \leftrightarrows Ca(OH)_2.$$

The product is a bulky powder. The action is accompanied by the development of much heat. The change is reversible, and at a high temperature the hydroxide can be dehydrated.

Calcium hydroxide is slightly soluble in water, — 1 part in 600 parts of water at 18°, about twice as much water being required at 100°. The solution, relatively to its concentration, is strongly alkaline. On account of its cheapness, this substance is used by manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. Some of the industries in which caustic lime plays a part are: the manufacture of alkalies (p. 363), bleaching powder, and mortar (see below), the removal of the hair from hides in preparation for tanning, and the purification of illuminating-gas (p. 340).

Mortar and Cement. — Mortar is made by mixing water with slaked lime and a large proportion of sand. The "hardening" process consists in an interaction of the carbon dioxide of the air with the calcium hydroxide:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O.$$

After the superficial parts have been changed, the process goes on very slowly, and many years are required before the deeper layers have been transformed. The minute crystals of calcium carbonate which are formed are interlaced with the sand particles, and a rigid mass is finally produced. The "hardening" does not begin until the excess of water used in making the mortar has evaporated, and hence ordinary mortar is unsuitable for use in damp places such as cellars.

Cement is made by strongly heating a mixture of limestone, clay, and sand, and pulverizing the product. When the cement is mixed with water, it gradually sets to a solid mass which appears to consist of a mixture of silicates of calcium and aluminium. Since the change is not dependent on access of any gas, it proceeds throughout the whole material simultaneously, and not, as in the case of mortar from the surface inwards. For this reason the hardening of cement occurs just as well under water as in any other locality.

illustrate the application of ion-product co
explaining the phenomenon. The same expl
precipitations.

The first thing to be remembered is that the
observe, however insoluble its material may b
of the substance, but only the excess beyond
saturate the water. **The liquid surrounding the
saturated solution of the substance precipitated.**
some of the precipitate would dissolve unti
saturated. Thus, for example, when we add
solution to calcium chloride solution:

$$\left.\begin{array}{l}(NH_4)_2C_2O_4 \leftrightarrows 2NH_4^{\cdot} + C_2O_4^{''} \\ \quad CaCl_2 \leftrightarrows 2Cl' \quad + \quad Ca^{\cdot\cdot}\end{array}\right\} \leftrightarrows CaC_2O_4 \text{ (dslv}$$

the liquid is a saturated solution of calcium oxa
of this salt suspended in it.

Looking at the matter from this view-point, w
cation of the rule of ion-product constancy. In
tion (p. 384) the product of the ion-concentratio
is constant. If the original solutions had been
when they were mixed, the product of the con
two ions had not reached the value of this consta
would have occurred. As a matter of fact the ion-p
exceeded the requisite value, and hence the sal
until the balance remaining gave the value in

Rule for Solution of Substances. — The **rule for solution** of ny ionogen follows at once from the foregoing considerations, and ay be formulated by changing a few of the words in the rule just ven: **Whenever the product of the concentrations of any two ions in a xture *is less than* the value of the ion-product in a saturated solution the compound formed by their union, this compound,** if present in the lid form, **will be *dissolved.*** When applied to the simplest case, is rule means that a substance will dissolve in a liquid not yet turated with it, but will not dissolve in a liquid already saturated ith the same material. The value of the rule lies in its application the less simple, but equally common cases, such as when an soluble body is dissolved by interaction with another substance next section).

Applications of the Rule for Solution to the Solution of Insoluble Substances. — So long as a substance remains in pure vater its solubility is fixed. Thus, with calcium hydroxide, the ystem comes to rest when .17 g. per 100 c.c. of water have gone into olution:

$$Ca(OH)_2 \text{ (solid)} \rightleftarrows Ca(OH)_2 \text{ (dslvd)} \rightleftarrows Ca^{\cdot\cdot} + 2OH'.$$

But if an additional reagent which can combine with either one of he ions is added, the concentration of this ion at once becomes less, he ion-product therefore tends to diminish, and further solution nust take place to restore its value. Thus, if a little of an acid giving $H^{\cdot}$) be added to the solution of calcium hydroxide, the union of OH' and $H^{\cdot}$ to form water removes the OH', and solution of the ydroxide proceeds until the acid is used up. There are now more $Ca^{\cdot\cdot}$ than OH' ions present, but the *ion-product* reaches the same alue as before, and then the change ceases. If a further supply of cid is added, the removal of OH' to form H_2O begins again. With *xcess of the acid*, the only stable OH' concentration is that which is factor in the very minute ion-product of water, $[OH'] \times [H^{\cdot}]$. Hence, the calcium hydroxide, which requires in general a much igher concentration of OH' than this to precipitate it or to keep it out of solution, finally all dissolves.

This particular action is a neutralization of an insoluble base. But the other kinds of actions by which insoluble ionogens pass into olution all resemble it closely, and differ only in details. The general outlines of the explanation are the same in every case. We

$$CaC_2O_4 \uparrow + 2HCl \rightleftarrows CaCl_2 + H_2C$$

The action of acids upon insoluble salts is so freq
chemistry and is so important a factor in analytic
demands separate discussion. This example is
may be used as an illustration.

According to the rules already explained (p. 39
(or any other salt) is precipitated when the pro
trations of the two requisite ions $[Ca^{\cdot\cdot}] \times [C_2O_4$
product for a saturated solution of calcium oxa
When, on the contrary, the product of the concen
ions falls below the limiting value, a condition wh
the removal in some way either of the $Ca^{\cdot\cdot}$ or of
undissociated molecules will ionize, and the sol
replace them until the ionic concentrations necess
with the molecules have been restored or until the
present is consumed. Here the oxalate-ion from
late combines with the hydrogen-ion of the acid
one) which has been added, and forms molecular

$$C_2O_4'' + 2H^{\cdot} \leftrightarrows H_2C_2O_4.$$

Hence, dissociation of the dissolved molecules of ca
ceeds, being no longer balanced by encounters and
depleted ions, and this dissociation in turn leads to
molecules from the precipitate.

It will be seen that the removal of the ions in

are is, however, a decisive factor in the situation which we have yet taken into account. The hydrochloric acid which we used dissolving the precipitate is a very highly ionized acid and gives enormously greater concentration of hydrogen-ion than does alic acid. Hence the hydrogen-ion is in excess in equation (2), d the condition of equilibrium for oxalic acid, $\frac{[H^{\cdot}]^2 \times [C_2O_4'']}{[H_2C_2O_4]} = K$, ll be satisfied by a correspondingly small concentration of C_2O_4''. this particular case, therefore, the $[C_2O_4'']$ of the oxalic acid *is* ss than that given by the calcium oxalate. The whole change, erefore, depends for its accomplishment not only on the mere resence of hydrogen-ion, but *on the repression of the ionization of the xalic acid* by the great excess of hydrogen-ion furnished *by the ctive acid* that has been used. As a matter of fact, we find that a eak acid like acetic acid has scarcely any effect upon a precipitate f calcium oxalate. An acid stronger than oxalic acid must be mployed. The whole scheme of the equilibria is as follows:

$$aC_2O_4(\text{solid}) \rightleftarrows CaC_2O_4(\text{dslvd}) \begin{matrix} \leftrightarrows Ca^{\cdot\cdot} + C_2O_4'' \\ 2HCl \quad \leftrightarrows 2Cl' + 2H^{\cdot} \end{matrix} \Big\} \rightleftarrows H_2C_2O_4(\text{dslvd}). \quad (3)$$

When excess of an acid sufficiently active to furnish a large concenration of hydrogen-ion is employed, the last equilibrium is then riven forward and the others follow. With addition of a weak acid, nly a slight displacement occurs, and the system comes to rest again hen the molecular oxalic acid has reached a sufficient concentration.

A **generalization** may be based on these considerations: **an insoluble alt of a given acid will in general interact and dissolve when treated vith a solution containing another acid, provided that the latter acid is a nuch more highly ionized (more active) one than the former** (see below).

But even active acids frequently fail to bring salts of weak acids nto solution, especially when the weak acid is itself present also. Iere the cause lies in the fact that such salts are less soluble than hose of the calcium oxalate type, and give so low a concentration f the negative ion that the utmost repression of the ionization of he corresponding acid does not give a lower value for the concenration of this ion than does the salt itself. Thus, we have seen p. 254) that even hydrochloric acid (dilute) will not dissolve a umber of sulphides. For example, in the case of cupric sulphide in solution saturated with hydrogen sulphide, the S'' factor in the

tends so decidedly backward that only the use o
will increase the concentration of the H^+ to an
secure any marked advance of the whole actio
therefore, to the above rule: **provided also that t
extreme insolubility.** This point will be illustr
connection with the description of individual su
Cadmium).

Illustrations of the application of these general
less. Carbonic acid is made from marble (p. 322),
from ferrous sulphide (p. 251), hydrogen pero
peroxide (p. 211), and phosphoric acid from
(p. 303). In each case the acid employed to dec
more active than the acid to be liberated. On th
cium oxalate is insoluble in acetic acid because t
than is oxalic acid. We have thus only to exami
showing their degrees of ionization (p. 228) in o
tell which salts, if insoluble in water, will be dissol
in general, what acids will be sufficiently active in
purpose. In chemical analysis we discrimina
soluble in water, those soluble in acetic acid (the in
and some sulphides, FeS and ZnS, for example)
active mineral acids for their solution (calcium oxa
insoluble sulphides, for example), and those inso
(barium sulphate and other insoluble salts of activ

phide or barium sulphate can be precipitated in presence of any d, but ferrous sulphide and calcium carbonate only in the absence acids.

From this it does not follow that calcium oxalate, for example, not be precipitated if once an active acid has been added to the xture. To secure precipitation, all that is necessary is to remove e excess of hydrogen-ion which is repressing the ionization of the alic acid. This can be done by adding a base, which removes the ", or even by adding sodium acetate. The acetate-ion $C_2H_3O_2'$ ites with the $H^{\cdot}$ to form the little ionized acetic acid, in presence which calcium oxalate can be precipitated.

Bleaching Powder Ca(OCl)Cl. — This substance (*cf.* p. 189) manufactured by conducting chlorine into a box-like structure ontaining slaked lime spread upon perforated shelves. When the ransformation has reached the limit (it is never complete), the upply of the gas is shut off, and some lime-dust is blown into the hamber to absorb the remainder of the free chlorine.

That bleaching powder is a mixed salt CaCl(OCl) rather than an equi-molar mixture of calcium chloride and calcium hypochlorite, which would have the same composition, $CaCl_2,Ca(OCl)_2$, is rendered probable by the facts that the material is not deliquescent as is calcium chloride, and that calcium chloride cannot be dissolved out of it by alcohol.

Bleaching powder is somewhat soluble in water, and in solution the ions $Ca^{\cdot\cdot}$, Cl', and ClO' are all present. Addition of active acids causes the formation of hydrochloric and hypochlorous acids (p. 193). Weak acids like carbonic acid displace the hypochlorous acid *only* (*cf.* p. 191), and hence the dry powder, when exposed to the air, has the odor of the latter substance rather than that of chlorine.

The substance is largely used by bleachers (*cf.* p. 193), and as a disinfectant to destroy germs of putrefaction and disease.

Calcium Sulphate. — This salt is found in large quantities in nature. The mineral **anhydrite** $CaSO_4$ occurs in the salt layers. It contains no water of crystallization, and its crystals belong to the rhombic system. The **dihydrate**, $CaSO_4,2H_2O$, is more plentiful. In granular masses it constitutes alabaster. When perfectly crystallized (monoclinic system, Fig. 35. p. 95) it is named **gypsum** or

selenite. The same hydrate is formed by precipitation from solu
Its solubility is about 1 in 500 at 18°.

Plaster of paris is manufactured by heating gypsum until
all the water of hydration has been driven out. When it is
with water, the dihydrate is quickly re-formed and a rigid
produced. That the plaster sets rapidly, is due to the fact th
anhydrous salt is more soluble than the dihydrate, and so a co
solution of the one and deposition of the other goes on until the
dration is complete. It becomes rigid, instead of forming a
mass of dihydrate, because the process results in the formatio
an interlaced and coherent mass of minute crystals.

$$CaSO_4 \text{ (solid)} \rightleftarrows \left.\begin{matrix} CaSO_4 \text{ (dslvd)} \\ 2H_2O \end{matrix}\right\} \rightleftarrows CaSO_4,2H_2O \text{ (solid)}.$$

Plaster of paris is used for making casts and in surgery. T
setting of the material is accompanied by a slight increase in volu
and hence a very sharp reproduction of all the details of the mold
obtained. An " ivory " surface, which makes washing practicab
is conferred by painting the cast with a solution of paraffin or stea
in petroleum ether. The waxy material, left by evaporation of t
volatile hydrocarbons, fills the pores and prevents solution
disintegration of the substance by water. Stucco is made w
plaster of paris and rubble, and is mixed with a solution of g
instead of water.

Calcium Sulphide CaS.—This compound is most easily ma
by strongly heating pulverized calcium sulphate and charcoal. T
sulphate is reduced:

$$4C + CaSO_4 \rightarrow CaS + 4CO.$$

Calcium sulphide is meagerly soluble in water, but is neverthe
slowly dissolved in consequence of its decomposition by hydrol
into calcium hydroxide and calcium hydrosulphide $Ca(SH)_2$ (*cf.*
254). Since calcium sulphide is thus decomposed by water it cann
be precipitated from aqueous solution by adding a soluble sulphi
such as ammonium sulphide, to a solution of a salt of calcium. On
the soluble hydrosulphide can be formed.

Ordinary calcium sulphide, after it has been exposed to sunligh
usually shines in the dark. Barium sulphide behaves in the sa

y. On this account these substances are used in making **luminous** nt. They apparently owe this behavior to the presence of traces compounds of vanadium and bismuth, for the purified substances e not affected in the same fashion.

Phosphates of Calcium. — The **tertiary orthophosphate of calcium** $Ca_3(PO_4)_2$, known as phosphorite, is found in many localities. is probably derived from the remains of animals. Guano contains ome of the same substance, along with compounds of nitrogen. **patite,** $3Ca_3(PO_4)_2,CaF_2$, a double salt with calcium fluoride, is a ommon mineral and frequent component of rocks. The orthophosphate forms about 83 per cent of bone-ash, and is contained also in he ashes of plants. It may be precipitated by adding a soluble hosphate to a solution of a salt of calcium.

Since it is a salt of a weak acid, and belongs to the less insoluble lass of such salts, calcium phosphate is dissolved by dilute mineral cids (*cf.* p. 397), the ions HPO_4'' and H_2PO_4' being formed. When a base, such as ammonium hydroxide, is added to the solution, the calcium phosphate is reprecipitated (*cf.* p. 398).

Calcium phosphate is chiefly used in the manufacture of phosphorus and phosphoric acid (p. 303), and as a fertilizer. The supply of calcium phosphate in the soil arises from the decomposition of rocks containing phosphates, and is gradually exhausted by the removal of crops. Bone-ash is sometimes used to make up the deficiency. It is almost insoluble in water, however, and, although somewhat less insoluble in natural water containing salts like sodium chloride, is brought into a condition for absorption by the plants too slowly to be of immediate service. In consequence of this the "superphosphate" (see below) is preferred.

Primary calcium orthophosphate ("superphosphate") is manufactured in large quantities from phosphorite by the action of sulphuric acid. The unconcentrated "chamber acid" is used for this purpose, as water is required in the resulting action. The amounts of material employed correspond to the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 6H_2O \rightarrow Ca(H_2PO_4)_2,2H_2O + 2CaSO_4,2H_2O.$$

As soon as mixture has been effected, the action proceeds with evolution of heat, and a large cake of the two hydrated salts remains. This mixture, after being broken up, dried, and packed in bags, is

sold as "superphosphate of lime." The primary phosphate it contains is soluble in water, and is therefore of great value fertilizer.

Calcium Silicate $CaSiO_3$.—Calcium metasilicate $CaSiO_3$ the mineral wollastonite, which is rather scarce, but enters into composition of many complex minerals, such as garnet and It may be made by precipitation with a solution of sodium silicate (p. 380), or by fusing together powdered quartz and carbonate:

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2.$$

Glass.—Common glass is a complex silicate of sodium and cium, or a homogeneous mixture of the silicates of these metals silica. It has a composition represented approximately by formula $Na_2O,CaO,6SiO_2$, and is made by melting together carbonate, limestone, and pure sand:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow Na_2O,CaO,6SiO_2 + 2CO_2.$$

For the most fusible glass, a smaller proportion of sand is emplo This variety is known, from its components, as **soda-glass**, or, its easy fusibility, as **soft glass**. Plate-glass is made by casting material in large sheets and polishing the surfaces until they plane. Window-glass is prepared by blowing bulbs of long c drical shape, and ripping them down one side with the help diamond. The resulting curved sheets are then placed on a surface in a furnace and are there allowed to open out. Bead made, chiefly in Venice, by cutting narrow tubes into very s sections and rounding the sharp edges by fire. Ordinary appa is made of soft soda-glass, and hence when heated strongly it t to soften and also to confer a strong yellow tint (*cf.* p. 380) o flame. Bottles are made with impure materials, and owe color chiefly to the silicate of iron which they contain. In all the articles are annealed by being passed slowly through a sp furnace in which their temperature is lowered very gradually. which has been suddenly chilled is in a state of tension and b easily when handled.

Soft glass is partially dissolved by water. When powdered is shaken with water, the liquid soon dissolves enough so

icate to give an alkaline reaction with phenolphthaleïn (*cf.* p. 2).

Bohemian, or **hard glass**, is much more difficult to fuse than soda-ass, and is also much less soluble in water. It is manufactured by bstituting potassium carbonate for the sodium carbonate. When ad oxide is employed instead of limestone, a soda-lead glass known **flint glass** is produced. This has a high specific gravity, and a eat refracting power for light, and is employed for making glass naments. By the use of grinding machinery, **cut glass** is made om it.

Colored glass is prepared by adding small amounts of various xides to the usual materials. The oxides combine with the silica, nd produce strongly colored silicates. Thus, cobalt oxide gives a lue, chromium oxide or cupric oxide a green, and uranium oxide a ellow glass. Cuprous oxide, with a reducing agent, and compounds f gold, give the free metals, suspended in colloidal solution (p. 96) n the glass, and confer a deep-red color upon it. Milk-glass contains inely powdered calcium phosphate in suspension, and white enamels are made by adding stannic oxide.

Glass is a typical amorphous substance (pp. 84, 249). From the facts that it has no crystalline structure, and that it softens gradually when warmed, instead of showing a definite melting-point, it is regarded as a supercooled liquid of extreme viscosity. Most single silicates crystallize easily, and have definite freezing- (and melting-) points. Glass may be regarded as a solution of several silicates. When kept for a considerable length of time at a temperature insufficient to render it perfectly fluid, some of its components crystallize out, the glass becomes opaque, and "devitrification" is said to have occurred. The word "crystal" popularly applied to glass is thus definitely misleading.

Calcium-ion: Analytical Reactions. — Ionic calcium $Ca^{\cdot\cdot}$ is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcium-ion in qualitative analysis (see p. 440). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope.

electrolysis of the molten chloride.

Compounds of Strontium. — The compounds
the natural carbonate or sulphate. The former
directly in acids, and the latter is first reduced by
to the sulphide, and then treated with acids.

Strontium chloride $SrCl_2,6H_2O$, made in one of t
deposited from solution as the hexahydrate. Th
comes out of hot solutions in octahedrons whic
From cold water the tetrahydrate $Sr(NO_3)_2,4H_2O$
anhydrous nitrate is mixed with sulphur, charco
chlorate to make "red fire." The **oxide** SrO m
igniting the carbonate, but it is obtained with grea
is calcium oxide from calcium carbonate. It is g
heating the nitrate or hydroxide.

Strontium hydroxide $Sr(OH)_2$ is made by heating
a current of superheated steam:

$$SrCO_3 + H_2O \rightarrow Sr(OH)_2 + CO_2.$$

This action takes place more easily than does the
of the carbonate, because the formation of the hy
energy, and this partially compensates for the ene
be provided to decompose the carbonate. The
partial pressure of the carbon dioxide by the steam
to the result (*cf.* p. 391). A hydrate $Sr(OH)_2,8H_2O$

BARIUM Ba.

The physical and chemical properties of the compounds of barium all those of strontium and calcium. All the compounds of barium ich are soluble in water, or can be brought into solution by the ak acids of the digestive fluids, are poisonous.

Occurrence. — Like strontium, barium is found in the form of carbonate, witherite $BaCO_3$, and the sulphate $BaSO_4$, heavy-spar barite (Gk. βαρύς, heavy). The free metal, which is silver-white, ay be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate with ids directly, or by first reducing the sulphate with carbon to sulide, or converting the carbonate into oxide, and then treating e products with acids.

Compounds of Barium. — The precipitated form of **barium rbonate** $BaCO_3$ is made by adding sodium carbonate to the aqueous xtract from crude barium sulphide (*q.v.*). Barium carbonate emands so high a temperature (about 1500°) for the attainment of sufficient dissociation tension, that special means is employed for s decomposition. It is heated with powdered charcoal (*cf.* p. 325):

$$BaCO_3 + C \rightarrow BaO + 2CO.$$

Natural **barium sulphate** $BaSO_4$ is the source of many of the comounds. The precipitated sulphate, made by adding sulphuric acid the aqueous extract from barium sulphide, is used in making hite paint ("permanent white"), in filling paper for glazed cards, nd sometimes as an adulterant of white lead. The salt is highly soluble in water and is hardly at all affected by aqueous solutions f any chemical agents.

Barium sulphide BaS, like the sulphides of calcium and strontium p. 400), is very slightly soluble in water, but slowly passes into olution owing to hydrolysis and formation of the hydroxide and ydrosulphide. It is made by heating the pulverized sulphate with harcoal:

$$BaSO_4 + 4C \rightarrow BaS + 4CO.$$

Barium chloride $BaCl_2,2H_2O$ is manufactured by heating the sulhide with calcium chloride. The whole treatment of the heavypar is carried out in one operation:

$$BaSO_4 + 4C + CaCl_2 \rightarrow 4CO + BaCl_2 + CaS.$$

By rapid treatment with water, the chloride can b
the calcium sulphide before much decomposition of
376) has taken place.

Barium chlorate $Ba(ClO_3)_2$ is made by treating
barium carbonate with a solution of chloric acid.
beautiful monoclinic crystals, and is used with sulp
in the preparation of "green fire."

Barium monoxide BaO is manufactured from th
above) or, in pure form, by heating the nitrate. T
vigorously with water to form the hydroxide.

The monoxide, when heated in a stream of air
barium peroxide BaO_2, as a compact gray mass. T
its reversal constitute the basis of Brin's process for o
from the air (p. 46). A **hydrate**, $BaO_2,8H_2O$, is th
crystalline precipitate when hydrogen peroxide solu
a solution of barium hydroxide:

$$Ba(OH)_2 + H_2O_2 \rightleftarrows BaO_2 \downarrow + 2H$$

Barium peroxide is used in the manufacture of hydr

Barium hydroxide $Ba(OH)_2$, is made by union of
water, or by leading moist carbon dioxide over th
decomposing the resulting carbonate with superhea
is the most soluble of the hydroxides of this group, a
fore, the highest concentration of hydroxide-ion.
known as "baryta-water." It is also the most stal
hydroxides, and may be melted without decompositi
$Ba(OH)_2,8H_2O$ crystallizes from water.

Barium nitrate $Ba(NO_3)_2$ is made by the action o
the sulphide, oxide, hydroxide, or carbonate of
crystals from aqueous solution are anhydrous.

Analytical Reactions of the Calcium Family.
$Ba^{\cdot\cdot}$ is a colorless, bivalent ion. Many of its compoun

phate solution precipitates barium sulphate, and does not give y result with salts of the first two. The oxalate of calcium is ecipitated in presence of acetic acid, while the oxalates of stron- ım and barium are not (*cf.* p. 398), and there are other differ- ıces of a like nature in the solubilities of the salts.

Exercises. — 1. Arrange the chromates of the metals of this ımily in the order of solubility (see Table). Compare the solubili- ıes with those of the carbonates, oxalates, and sulphates of the ıetals of the same family.

2. What is meant by fluorescence (*cf.* any book on physics)?

3. What will be the ratio by volume, at 150°, of the nitrogen per- xide and oxygen given off by the decomposition of calcium nitrate? What would be the nature of the difference between the ratio at 150° and that at room temperature (*cf.* p. 144)?

4. Apply the rule of precipitation to the case of adding sodium carbonate to a solution of barium chloride.

5. Explain in terms of the ionic hypothesis the precipitation of the sulphate of strontium by calcium sulphate solution, and the absence of precipitation when the latter is added to a dilute solution of a soluble salt of calcium.

6. What inference do you draw from the fact that the oxalates of barium and strontium are not precipitated in presence of acetic acid, while the oxalate of calcium is so precipitated? Is the inference confirmed by reference to the solubility data?

7. Explain the fact that strontium and calcium chromates are easily dissolved by acetic acid, while barium chromate is dissolved only by active mineral acids.

8. Explain the fact that all the carbonates, save those of potassium, sodium, and thallium, are precipitated in neutral solutions, but not in acidified solutions. Why is the precipitation incomplete when carbon dioxide is led through solutions of salts of the metals, but more complete when the hydroxides of the metals are used?

9. Construct a table for the purpose of comparing the properties of the free elements of this family and also the properties of their corresponding compounds.

10. Are the elements of this family typical metals (p. 353)?

CHAPTER XXXVI

COPPER, SILVER, GOLD

[illegible] metals of this family, being found free in [illegible] which were known in early times. They [illegible] usually used for coinage and for ornament [illegible] best conductors of electricity (p. 35[illegible]).

[illegible] ***Relations of the Copper Family.***—[illegible] silver (Ag, at. wt. 107.93), and gold [illegible] right side in the second column of the [illegible] the chemical relations of these [illegible] sharp contrast to those of the alkali [illegible] the left side:

[illegible]	COPPER, SILVER, GOLD
[illegible] by air. [illegible]	Amongst least active metals. copper is oxidized by air [illegible] by most other metals.
[illegible]	Cu^{I} and Cu^{II}: two series. Ag [illegible] series. Au^{I} and Au^{III}: two [illegible] Chlorides of univalent series [illegible]
[illegible]	Oxides and hydroxides feebly [illegible] (except Ag_2O); halides hy[illegible] (except Ag-halides). Hence [illegible] salts are numerous.
[illegible]	Frequently in anion, *e.g.*, $K_2Cu[illegible]$ $K[Ag(CN)_2]$, K_2AuO_2, $K_3Au[illegible]$ and in complex cations, *e.g.*, $Ag(NH_3)_2OH$ and $Cu(NH_3)_4[illegible]$

[illegible] towards oxygen, and their [illegible] of heat, silver and [illegible] known as the "noble me[illegible]

[illegible]

[illegible] ***ment.***—Copper is the [illegible] which we have encoun[illegible] independent series of [illegible] distinguished as cuprous (univ[illegible]

. cupric (bivalent) salts. The methods by which a compound of series may be converted into the corresponding compound of the er series should be noted.

The chief cuprous compounds are Cu_2O, CuCl, CuBr, CuI, CuCN, S. There are no cuprous salts of oxygen acids. The cuprous npound is in each case more stable (p. 81) than the corresponding pric compound, and is formed from it either by spontaneous composition, as in the cases of the iodide and cyanide ($2CuI_2$ $2CuI + I_2$), or on heating. The cuprous halides and cyanide e colorless and insoluble in water. Cuprous-ion $Cu^{\cdot}$ seems to colorless.

The cupric compounds are more numerous, as they include also lts of oxygen acids, like $CuSO_4$, $Cu(NO_3)_2$, etc. The anhydrous lts are usually colorless or yellow, but cupric-ion $Cu^{\cdot\cdot}$ is blue, and , therefore, are the aqueous solutions of the salts. The cupric are ore familiar than the cuprous compounds, since cupric oxide, ulphate, and acetate are the compounds of copper which most equently find employment in chemistry and in the arts. All the oluble salts of copper are poisonous.

Occurrence. — Copper is found free in the Lake Superior region, n China, and in Japan. The sulphides, copper pyrites $CuFeS_2$ and halcocite Cu_2S, are worked in Montana, in southwest England, in pain, and in Germany. Malachite, $Cu_2(OH)_2CO_3$ ($= Cu(OH)_2$, $CuCO_3$), a basic carbonate, is mined in Siberia and elsewhere. uprite or ruby copper Cu_2O is also an important ore.

Extraction from Ores. — For isolating native copper it is only ecessary to separate the metal, by grinding and washing, from the ock through which it ramifies, and to melt the almost pure powder f copper with a flux (p. 355). The carbonate and oxide ores require oal, in addition, for the removal of the oxygen.

The liberation of copper from the sulphide ores is difficult, and ften involves very elaborate schemes of treatment. This arises rom the fact that many copper ores contain a large amount of the ulphides of iron, and these have to be removed by conversion into xide (by roasting) and then into silicate (with sand). The silicate orms a flux, and separates itself from the molten mixture of copper nd copper sulphide. In Montana it is found possible to abbreviate he treatment. The ore is first roasted until partially oxidized. It

the converter are poured out. The resulting coppe
to be cast in large plates and purified by electrolysi

Wet processes are used for poor ores. In one of
roasted with salt. The copper is thus converted into
and can be dissolved away from the oxide of iron and
by means of water. Any traces of silver which
present pass also into solution (as AgCl), and are
addition of potassium iodide. The copper is the
means of scrap iron, and forms a brown sludge (Cu
+ Cu ↓).

The tenacity, ductility, and conductivity of copp
affected by small amounts of impurities, such as c
sulphide, which are soluble in the molten metal.
proportion of the copper on the market is purified
In this method of refining the metal, thin sheets of
cathodes, and thick plates of copper the anodes.
pended alternately and close together in large trou
cupric sulphate solution. The cathodes are all conn
negative wire of the dynamo, and the anodes with th
The $Cu^{\cdot\cdot}$ is attracted to the cathodes and is deposit
The SO_4'' migrates towards the anodes, where copper
plate becomes ionized in equivalent amount. The
sulphate thus remains the same, and the practica
electrolysis is to carry copper across from one plate
The cathodes are removed from time to time, and
copper is stripped from their surface. Fresh anodes

In ordinary air copper becomes slowly covered with a green basic carbonate (*not* verdigris, *q.v.*). It does not decompose water at any temperature or displace hydrogen from dilute acids (p. 245). The metal attacks oxygen acids (pp. 257, 298), however. Sea-water and air slowly corrode the copper sheathings of ships, giving a basic chloride, $Cu_4(OH)_6Cl_2, H_2O$ (= $3Cu(OH)_2, CuCl_2, H_2O$), which is found in nature as atakamite.

On account of its resistance to the action of acids, copper is used for many kinds of vessels, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. For this purpose a cast of the object is first made in gutta percha, plaster of paris, or wax. This is then coated with graphite to give it a conducting surface, and receives an electrolytic deposit of copper. Great quantities of the metal are used in electrical plants and appliances.

Alloys. — The qualities of copper are modified for special purposes by alloying it with other metals. **Brass** contains 18–40 per cent of zinc, and melts at a lower temperature (p. 390) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch-metal (" gold-leaf "). **Bronze** contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast-iron (discovered in the eighteenth century). **Gun-metal** contains 10 per cent, and **bell-metal** 25 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper.

Cupric Chloride $CuCl_2, 2H_2O$. — This compound is made by union of copper and chlorine, or by treating the hydrate or carbonate with hydrochloric acid. The blue crystals of a **hydrate**, $CuCl_2,2H_2O$, are deposited by the solution. The **anhydrous salt** is yellow. Dilute solutions are blue, the color of cupric-ion, but concentrated solutions are green on account of the presence of the yellow molecules (p. 227). The aqueous solution is acid in reaction (p. 353). When excess of ammonium hydroxide is added to the solution, the basic chloride, **cupric oxychloride** $Cu_4(OH)_6Cl_2$ (above), which is at first precipitated, redissolves, and a deep-blue solution is obtained (see p. 413). This

on evaporation yields deep-blue crystals of hydrated chloride $Cu(NH_3)_4.Cl_2,H_2O$. The deep-blue color of which is given by all cupric salts, is that of amm $Cu(NH_3)_4^{\cdot\cdot}$. The dry salt also absorbs ammonia, givi but a reduction of pressure results in the final loss of al

Cuprous Chloride CuCl.—It may be made by chloric acid to cupric chloride solution, and boiling th copper turnings:

$$CuCl_2 + Cu \rightarrow 2CuCl \quad \text{or} \quad Cu^{\cdot\cdot} + Cu \rightarrow 2$$

The solution contains compounds of cuprous chloride chloride HCl,CuCl or $HCuCl_2$ and H_2CuCl_3, which ar when water is added. The cuprous chloride is insol and forms a white crystalline precipitate.

The foregoing action is an illustration of the fifth chemical change, namely that in which a change in val in the amount of the electrical charge), occurs, without in the composition of the ionic substance. For othe see pp. 111 ($Mn^{\cdot\cdot\cdot\cdot} + 4Cl' \rightarrow Mn^{\cdot\cdot} + 2Cl' + Cl_2$), 409.

Cuprous chloride is hydrolyzed quickly by hot finally, red, hydrated cuprous oxide, Cu_2O. When affected by light, but in the moist state becomes violet nearly black. The action is said to be $2CuCl \rightarrow Cu$ moist air it turns green, and is oxidized to cupric oxychl It is dissolved by hydrochloric acid, giving the colo acids $HCuCl_2$ and H_2CuCl_3 (see p. 413). The solution i the air, turning first brown and then green, and final the cupric oxychloride. Cuprous chloride also dissolv nium hydroxide (see p. 413), giving ammonio-cup $Cu(NH_3)_2.Cl$, the ion $Cu(NH_3)_2^{\cdot}$ being colorless. Th quickly oxidized by the air, turns deep-blue, and t $Cu(NH_3)_4^{\cdot\cdot}$.

When a soluble iodide is added to a cupric salt, a white precipitate of cuprous iodide CuI and free iodine are obtained:

$$2Cu^{\cdot\cdot} + 4I' \leftrightarrows 2CuI \downarrow + I_2.$$

The Solution of Insoluble Salts when Complex Ions are Formed. — The solution of an insoluble salt like cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions of which we here meet with the first examples (*cf.* p. 253).

The dissolving of cuprous chloride in hydrochloric acid (p. 412), to form soluble complex acids like $H.CuCl_2$, requires a special explanation. The complex negative ion $CuCl_2'$ which is formed, is very little dissociated ($CuCl_2' \rightleftarrows Cu^{\cdot} + 2Cl'$), and gives a smaller concentration of $Cu^{\cdot}$ than does the insoluble cuprous chloride. Thus, this complex ion is formed at the expense of the $Cu^{\cdot}$ of the insoluble cuprous chloride, and the latter goes into solution progressively in the effort to restore the balance:

$$\begin{array}{l} CuCl\ (solid) \leftrightarrows CuCl\ (dslvd) \leftrightarrows Cl' + Cu^{\cdot} \\ \qquad\qquad\qquad 2HCl \qquad\quad \leftrightarrows 2H^{\cdot} + 2Cl' \end{array}\Bigg\} \rightleftarrows CuCl_2'\ (dslvd).$$

The same exact laws of equilibrium used in discussing the dissolving of salts by acids (p. 396) may be applied to the whole procedure.

The dissolving of cuprous chloride by the free ammonia of ammonium hydroxide is explained in the same way. The only difference is that here the copper is in a complex positive ion. The ion $Cu(NH_3)_2^{\cdot}$ gives little $Cu^{\cdot}$ — less than does cuprous chloride, in spite of the insolubility of the latter. Hence the salt passes into solution until the ion-product $[Cu^{\cdot}] \times [Cl']$, with continually increasing $[Cl']$, reaches its normal value or until the solid is exhausted.

The deep-blue colored ion $Cu(NH_3)_4^{\cdot\cdot}$ given by cupric chloride and other cupric salts is also very little ionized. Hence ammonium hydroxide dissolves all the insoluble cupric compounds save only cupric sulphide, which is the most insoluble of all — that is, the one giving the smallest concentration of cupric-ion. Conversely, the sulphide is the only insoluble compound of copper which can be precipitated from ammoniacal solution.

Cuprous Oxide Cu_2O. — This oxide is red in color, and natural specimens show octahedral forms. It is produced by oxidation of

Cuprous oxide is dissolved upon by hydrochloric acid
chloride, or rather $HCuCl_2$. It also dissolves in amm
giving, probably, $Cu(NH_3)_2.OH$, which is colorless.

Cupric Oxide and Hydroxide. — **Cupric oxid**
substance formed by heating copper in a stream
igniting the nitrate, carbonate, or hydroxide. Whe
it loses some oxygen, and is partly reduced to cupr

Cupric hydroxide $Cu(OH)_2$ is precipitated as a gel
by addition of sodium or potassium hydroxide to
cupric salt ($Cu^{\cdot\cdot} + 2OH' \rightarrow Cu(OH)_2$). When the
the hydroxide loses water and forms a black hydr
($Cu(OH)_2.2CuO$?). The hydroxide is soluble in am
ide, with formation of the compound $Cu(NH_3)_4.(OH$
a deep-blue color to the solution.

Cupric Nitrate $Cu(NO_3)_2,6H_2O$. — The nitr
treating cupric oxide or copper with nitric acid
obtained from the solution as a deliquescent, crystal
When dehydrated at 65° the salt is partly hydroly
nitrate $Cu_4(OH)_6(NO_3)_2$ remains.

Carbonate of Copper. — No normal carbonate
obtained. A **basic carbonate** (malachite) is found i
precipitated by adding soluble carbonates to cupric
$2CuSO_4 + 2Na_2CO_3 + H_2O = Cu_2(OH)_2CO_3 + 2N$

prous cyanide is insoluble in water, but interacts with an excess of tassium cyanide solution, producing a colorless liquid, from which $Cu(CN)_2$ (= KCN,CuCN), **potassium cuprocyanide**, may be obtained colorless crystals. The complex anion $Cu(CN)_2'$ is so little ionized Cu· and 2CN′ that all insoluble copper compounds, *including pric sulphide*, are dissolved by potassium cyanide; and none of iem can be precipitated from the solution. Zinc is actually unable displace copper from such a solution. The cause of the solution the salts is the same as when the complex ions $Cu(NH_3)_2^{\cdot}$, $u(NH_3)_4^{\cdot\cdot}$, and $CuCl_2'$ are formed (p. 413).

Cupric Acetate.— By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:

$$6Cu + 8HC_2H_3O_2 + 3O_2 \rightarrow 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O.$$

It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the **normal acetate** $Cu(C_2H_3O_2)_2,H_2O$ are obtained from the solution. The basic acetate is used in preparing **paris green**.

Cupric Sulphate $CuSO_4$. — This salt is obtained by heating copper in a furnace with sulphur, and admitting air to oxidize the cuprous sulphide. The mixture of cupric sulphate and cupric oxide which is formed is treated with sulphuric acid. The salt is also made by allowing dilute sulphuric acid to trickle over granulated copper while air has free access to the material:

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O.$$

This is an example of the use of two reagents which separately have little or no action (*cf.* pp. 344–345). When concentrated and at a high temperature, sulphuric acid will itself act as the oxidizing agent (*cf.* p. 263).

Cupric sulphate crystallizes as **pentahydrate** $CuSO_4,5H_2O$ in blue asymmetric crystals (Fig. 26, p. 82), and in this form is called **bluestone** or **blue vitriol**. The aqueous solution has an acid reaction (p. 353). The anhydrous salt is white, and can be crystallized in thin needles from solution in hot, concentrated sulphuric acid (*cf.* p. 82). Cupric sulphate is employed in copper-plating (p. 410), in

Cupric sulphate also combines with potassium sulphates, giving **double salts** of the form $CuSO_4,K_2$ are deposited in large, monosymmetric crystals solutions. Double salts (p. 231) exist as such in th and, in water, are resolved into their components.

The Sulphides of Copper. — **Cuprous sulphid** nature in rhombic crystals of a gray, metallic a made by heating cupric sulphide, a stream of hydrog to assist the removal of the excess of sulphur.

Cupric sulphide CuS is deposited as a black hydrogen sulphide is led through a solution of a cu in this way, it is always partly decomposed into cautiously treating copper with excess of sulphur a obtained as a blue crystalline solid. At higher gives off sulphur.

Analytical Reactions of Compounds of Co of ordinary cupric salts, cupric-ion $Cu^{\cdot\cdot}$, is blue, and salts, cuprous-ion $Cu^{\cdot}$, is colorless. Cuprous solutio easily oxidized by the air and become blue. In solu cupric-ion, hydrogen sulphide precipitates cupric su presence of acids (p. 398). Bases throw down the and carbonates precipitate a green basic salt (p. 41 ferrocyanide gives the brown, gelatinous **cupric ferro**

rocosmic salt or borax (pp. 312, 350), copper compounds form a d which is blue in the oxidizing part of the flame and becomes l and opaque (liberation of copper) in the reducing flame.

SILVER.

Chemical Relations of the Element. — This element presents curious assortment of chemical properties. It differs from copper having a strongly basic oxide, and in giving salts with active acids hich are not hydrolyzed by water. In these respects it approaches e metals of the alkalies and alkaline earths. It resembles copper entering into complex compounds, and in giving insoluble halides. t differs from both copper and the metals of the alkalies, and esembles gold and platinum, in that its oxide is easily decomposed y heat, with formation of the free metal, and in the low position it ccupies in the electromotive series and the consequent slight chemcal activity of the free metal.

Occurrence. — Native silver, usually scattered through a rocky natrix, contains varying amounts of gold and copper. Native opper always contains dissolved silver. Sulphide of silver (Ag_2S) ccurs alone and dissolved in galenite (PbS). Smaller amounts of he metal are obtained from pyrargyrite Ag_3SbS_3 and proustite Ag_3AsS_3, and from horn-silver AgCl.

Metallurgy.—The silver contained free, or as sulphide, in ores of opper and lead, is found in the free state dissolved in the metals xtracted from these ores, and is secured by refining them. In the lectrolytic refining of copper, silver is obtained from the mud leposited in the baths (p. 410). The proportion present in lead is sually small. **Parke's process**, by which the silver is separated from he lead, takes advantage of the fact that molten zinc and lead are ractically insoluble in one another, while silver is much more oluble in zinc than in lead. Lead dissolves 1.6 per cent of zinc, and inc 1.2 per cent of lead. The principle is the same as in the removal f iodine from water by ether (p. 103). The lead is melted and horoughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it in olution almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy is skimmed off,

and heated moderately in a furnace to permit the adhering lead to drain away. The zinc is finally distilled off in clay retorts, and the lead remaining with the silver is removed by cupellation. This operation consists in heating the molten metal strongly in a blast of air. The lead is converted into litharge (PbO), which flows in molten condition over the edge of the cupel.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as described above, but many other processes are in use. Thus, sulphide ores are sometimes roasted until the iron and part of the copper are converted into oxide while the rest of the copper and all the silver remain as sulphate. The metal is secured by extracting the mass with water and precipitating the silver by means of copper (p. 245). Some ores are roasted with salt, and the resulting chloride of silver is dissolved out with sodium thiosulphate, or even strong brine.

During the first half of the nineteenth century the world's total output of silver averaged only 643 tons per year. Up to 1870 a gram of gold could buy 15.5 g. of silver. Now that the production has reached 6000 tons, the same amount of gold purchases about 35 g.

Physical Properties. — Pure silver is almost perfectly white. It melts at 960°. Its ductility is so great that wires can be drawn of such fineness that 2 kilometers weigh only about 1 g. In the molten condition it absorbs mechanically about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

By addition of ferrous citrate to silver nitrate, a red solution and lilac precipitate of free silver can be made. The latter, after washing with ammonium nitrate solution, gives a red, colloidal solution in water. Such colloidal solutions of metals are formed also by passing an electrical discharge between wires of silver, gold, or platinum held under water.

Silver is alloyed with copper to render it harder. The silver coinage of the United States and the continent of Europe has a "fineness of 900" (900 parts of silver in 1000), and that of Great Britain 925. Silver ornaments have a fineness of 800 or more.

Chemical Properties. — Silver does not combine, with oxygen either in the cold or when heated. It does not ordinarily displace hydrogen from aqueous solutions of acids. Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (pp. 257, 298).

The Halides of Silver. — The **chloride** AgCl, **bromide** AgBr, and **iodide** AgI are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about 457°. The second and third are very pale-yellow and yellow respectively. The insolubility in water, which is very great, increases in the above order.

When exposed to light, the chloride becomes first violet and finally brown, chlorine being liberated. The bromide and iodide behave similarly. Solid silver chloride absorbs ammonia, forming first $2AgCl,3NH_3$, and then $AgCl,3NH_3$.

Complex Compounds of Silver. — Silver chloride dissolves easily in excess of ammonium hydroxide, giving the complex cation $Ag(NH_3)_2^{\cdot}$. The bromide, which is less readily soluble, gives the same complex ion. The iodide is hardly soluble at all. Ammonio-argentic-ion $Ag(NH_3)_2^{\cdot}$, in solutions of concentrations such as are commonly used (.1 *N* to *N*), gives about the same concentration of argention $Ag^{\cdot}$ as does the bromide, and much more than the highly insoluble iodide (*cf.* p. 413). Hence the latter is almost insoluble in ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides dissolve in solutions of potassium cyanide and of sodium thiosulphate, as do also all the other insoluble silver salts. Usually an equivalent amount of the cyanide or thiosulphate suffices, but for solution of the sulphide an excess is required. With the cyanide, double decomposition gives first the insoluble silver cyanide (AgCN) which then dissolves, forming the soluble **potassium argenti-cyanide** $K.Ag(CN)_2$. The thiosulphate gives a solution containing the complex salt $Na_3.Ag(S_2O_3)_2$. The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

Oxides of Silver. — When sodium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained,

which, after being freed from water, is found to be **argentic oxide** Ag_2O, and not AgOH. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide: $2AgOH \rightleftarrows Ag_2O + H_2O$.

Argentic oxide melts and gives off its oxygen at 250–270°. It is an active basic oxide. When moist, it absorbs carbon dioxide from the air. With ammonium hydroxide it forms the soluble $Ag(NH_4)_2.OH$.

Silver **peroxide** Ag_2O_2 is formed by the action of ozone on silver. In the electrolysis of silver nitrate it is deposited in shining black crystals on the anode. There is also a **suboxide** Ag_4O.

Salts of Silver. — **Silver nitrate** $AgNO_3$ is obtained by treating silver with aqueous nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

From the solution, colorless rhombic crystals (Fig. 7, p. 8) are deposited. These melt at 218°. In the form of thin sticks made by casting (lunar caustic), the substance is used in medicine, partly because it combines with albumins to form insoluble compounds. The aqueous solution is neutral. The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is converted into the chloride, and from this, in turn, silver is liberated. For this reason it is an ingredient in some marking-inks.

Silver carbonate, the neutral salt Ag_2CO_3, and not a basic carbonate, is precipitated from solutions of salts of silver by soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction, and, like calcium carbonate, is soluble in excess of carbonic acid (p. 391). When heated, the carbonate decomposes, leaving metallic silver. The **sulphate** Ag_2SO_4 is made by the action of concentrated sulphuric acid on the metal. When it is mixed with a solution of aluminium sulphate (*q.v.*), octahedral crystals of **silver-alum** $Ag_2SO_4.Al_2(SO_4)_3.24H_2O$ are obtained. **Silver sulphide** Ag_2S is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. Excess of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the basis of the " hepar "

test for sulphur. Silver **orthophosphate** Ag_3PO_4 (yellow), **arsenate** Ag_3AsO_4 (brown), and **chromate** Ag_2CrO_4 (crimson), are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

Electroplating. — The process is similar to the electro-deposition of copper (p. 410). The article to be plated is cleaned with extreme care and attached to the negative wire. A plate of silver forms the positive electrode and, since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The potassium-ion ($K^{\cdot}$) migrates to the negative wire and, since potassium requires a much greater E.M.F. for its liberation than does silver, silver is there deposited from the trace of argentic-ion given by the complex silver ions in the neighborhood:

$$Ag(CN)_2' \leftrightarrows Ag^{\cdot} + 2CN', \quad Ag^{\cdot} + \ominus \rightarrow Ag.$$

At the positive electrode silver goes into solution in equivalent amount, giving argentic-ion, and the above equations are reversed.

Mirrors are silvered through the reduction of silver nitrate by organic compounds such as potassium-sodium tartrate (Rochelle salt), glycerine, formaldehyde (formalin), or grape sugar.

Photography. — Bromo-gelatine dry plates are covered with an emulsion of gelatine in which silver bromide is suspended.

After **exposure**, often for only a fraction of a second, there is no visible alteration in the film. The image is **developed**. Chemically, this consists in reducing the silver bromide to metallic silver by means of reducing agents. While the whole of the halide upon the plate is reducible, if the reducing agent is kept upon it for a sufficient length of time, the parts reached by the light are affected *first*, and with a speed proportional to the intensity of the illumination undergone by each part. The unreduced silver bromide is then dissolved out with sodium thiosulphate (" hyposulphite of soda " or " hypo "), and the silver image is thus saved from being fogged over by the silver that would be deposited if the plate were to be brought into the light without this treatment (**fixing**). The result is a " negative," as the parts brightest in the object are now opaque, and the darkest parts of the object are transparent.

The simplest developer is potassium-ferrous oxalate $K_2.Fe(C_2O_4)_2$, a solution of which may be made by mixing ferrous sulphate and

potassium oxalate. For the sake of simplicity we may regard the action as a reduction by means of ferrous oxalate, which itself is oxidized to ferric oxalate ($Fe_2(C_2O_4)_3$):

$$3FeC_2O_4 + 3Ag_4Br \rightarrow Fe_2(C_2O_4)_3 + FeBr_3 + 3Ag.$$

In brief, we have $3Fe^{II}$ becoming $2Fe^{III} + Fe^{III}$, and this amount of bivalent iron therefore takes up 3Br, liberating the silver with which it was combined. The developers commonly employed are alkaline solutions of the sodium salts of hydroquinone and pyrogallic acid.

In printing, the light and dark are again reversed, the denser parts of the negative protecting the compounds on the paper below it from action, and leaving them white. Either " bromide " papers, which require only brief exposure and are developed like the plate, are used, or silver chloride is the sensitive substance, and prolonged exposure to light is allowed to liberate the proper amount of silver. The operation of fixing is performed as before. In toning, a solution of sodium chloraurate is employed. A portion of the silver dissolves, displacing gold (p. 245), which is deposited in its place:

$$NaAuCl_4 + 3Ag \rightarrow NaCl + 3AgCl + Au.$$

The thin film of gold gives a richer color to the print.

Analytical Reactions of Silver Compounds.—Argentic-ion $Ag^{\cdot}$ is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but silver chloride dissolves in ammonium hydroxide, mercurous chloride (*q.v.*) turns black, and lead chloride is not altered in color (and is also soluble in hot water). With excess of ammonium hydroxide, silver salts give the complex cation $Ag(NH_3)_2^{\cdot}$ and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 419).

Gold.

Chemical Relations of the Element. — This element forms two very incomplete series of compounds corresponding respectively to aurous and auric oxides, Au_2O and Au_2O_3. The former is a feebly basic oxide, the latter mainly acid-forming. No simple salts

with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 245). Mild reducing agents likewise liberate gold. The element enters into many complex anions.

Occurrence and Metallurgy. — Gold is found chiefly in the free condition disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron and copper. Telluride of gold (sylvanite), in which silver takes the place of a part of the gold $[Au,Ag]Te_2$, is found in Colorado.

From the alluvial deposits, gold is usually separated by washing in a cradle, as in the Klondyke. Quartz veins, which in the Transvaal Colony reach a thickness of a meter and carry an average of 18 g. of gold per ton, are mined, and the material is pulverized with stamping machinery. About 55 per cent of the gold is then separated by allowing the powdered rock to be carried by a stream of water over copper plates amalgamated with mercury. The gold dissolves in the latter, and is secured by removal and distillation of the amalgam. The finer particles, contained in the sludge which runs off (" tailings "), are extracted by adding a dilute solution of potassium cyanide (MacArthur-Forest process) and exposing the mixture to the air. Oxidation and simultaneous interaction with the cyanide give potassium aurocyanide $KAu(CN)_2$. From this solution the gold is isolated, either by electrolysis, or in the form of a purple powder by precipitation with zinc.

Auriferous pyrites is roasted, and then treated with chlorine gas. The chloride of gold which is formed is dissolved out with water. From the solution, the gold is precipitated with ferrous sulphate or oxalic acid:

$$2AuCl_3 + 6FeSO_4 \rightarrow 2Fe_2(SO_4)_3 + 2FeCl_3 + 2Au.$$

In the former case a purple powder, and in the latter, if the solution is heated, a spongy mass (the form used by dentists), is obtained.

The gold separated from ores in the above ways contains silver, copper, lead, and other metals, and various methods of refining, electrolytic and otherwise, are used. In one of these the gold is melted, and a stream of chlorine is passed through it. The metals, excepting gold, are converted into chlorides. The chloride of silver

rises as a liquid to the surface, while chlorides of arsenic and antimony are volatilized. A layer of melted borax prevents loss of silver chloride by volatilization. The silver chloride, when it has solidified, is placed between wrought-iron plates and immersed in an electrolyte (usually dilute sulphuric acid).

The world's production of gold during the first half of the nineteenth century averaged 27 tons annually. In 1897 it was 363 tons, and in 1899, 472.6 tons. In the former year North America, including Canada, produced 28.5 per cent of the whole, the Transvaal Colony 23.2 per cent, and Australia 21.2 per cent.

Properties of the Metal. — Gold is yellow in color, and is the most malleable and ductile of all the metals. It melts at 1064°. To give it greater hardness it is alloyed with copper, the proportion of gold being defined in "carats." Pure gold is "24-carat." British sovereigns are 22-carat and contain $\frac{2}{24}$ of copper. American, French, and German coins are 21.6-carat, or 90 per cent gold.

Gold is not affected by free oxygen nor by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it interact with nitric or sulphuric acids or any oxygen acids except selenic acid. It combines, however, with free chlorine, and it therefore interacts with a mixture of nitric and hydrochloric acids (*aqua regia*), which gives off this gas (p. 299). Chlorauric acid $H.AuCl_4$ ($= HCl,AuCl_3$) is formed, and the action is assisted by the fact that the gold ions are taken into the little-dissociated anion $AuCl_4'$. Gold is the least active of the familiar metals.

Compounds with the Halogens. — **Chlorauric acid**, formed as above, is deposited in yellow, deliquescent crystals of $H.AuCl_4,4H_2O$. The yellow sodium chloraurate $NaAuCl_4,2H_2O$, obtained by neutralization of the acid, is used in photography (p. 422). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride** $AuCl_3$. When auric chloride is heated to 180° **aurous chloride** AuCl and chlorine are formed. This salt is a white powder. It is insoluble in water, but in boiling water is converted quickly into auric chloride and free gold: $3AuCl \rightarrow AuCl_3 + 2Au$.

Other Compounds. — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide** $Au(OH)_3$ is precipitated. This substance is an acid, and interacts with excess of

the base, forming **aurates**. These are derived from met-auric acid ($Au(OH)_3 - H_2O = HAuO_2$), as, for example, **potassium aurate** $K.AuO_2,3H_2O$. This salt interacts by double decomposition, giving, for instance, with silver nitrate, the insoluble silver salt $AgAuO_2$. Its solution is alkaline in reaction, showing that auric acid is a weak acid (*cf.* p. 353).

Auric oxide Au_2O_3 is a brown, and **aurous oxide** Au_2O is a violet powder.

On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide** Au_2S and free sulphur, as well as some **auric sulphide** Au_2S_3.

The **aurocyanides**, like $K.Au(CN)_2$(= KCN,AuCN), and the **auricyanides**, like $K.Au(CN)_4$(=KCN,$Au(CN)_3$), are formed by the action of potassium cyanide on aurous and auric compounds, respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electrogilding.

Assaying.—In assaying, the material containing the gold is heated with borax and lead in a small crucible (cupel) of bone-ash. The lead and copper are oxidized, and the oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver and remove it completely if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy (" quartation ").

Exercises. — 1. Write equations for the interactions, (*a*) of salt water and oxygen with copper (p. 411), (*b*) of ferrous oxide and sand (p. 410).

2. Write the formulæ of the basic chloride, nitrate, carbonates, and sulphate of copper as if these substances were composed of the normal salt, the oxide and water (p. 411).

3. Can you develop any relation between the facts that solutions of cupric salts are acid in reaction and that they give basic carbonates by precipitation?

4. Formulate the action of potassium cyanide in dissolving cupric

hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

5. How should you set about making cupric orthophosphate (in solution), ammonium cuprocyanide, and lead cuprocyanide?

6. Write the formulæ of some of the double salts analogous to potassium-cupric sulphate (p. 416).

7. What chemical agents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

8. Write the equations for the interaction of, (*a*) silver and concentrated sulphuric acid, (*b*) silver chloride and sodium carbonate when heated strongly, (*c*) sodium thiosulphate and silver bromide.

9. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver?

10. Write the equations for the interactions of, (*a*) potassium hydroxide and auric hydroxide, (*b*) potassium cyanide and sodium chloraurate.

11. In what respects are the elements of this family distinctly metallic, and in what respects are they allied to the non-metals (p. 353)?

12. Collect all the evidence tending to show that the cuprous compounds are more stable than the cupric.

13. Make a classified list of the methods by which cupric compounds are transformed into cuprous, and *vice versa*.

14. Of which metals should it be possible to obtain colloidal solutions, and of which not (p. 245)?

CHAPTER XXXVII

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY. THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

The Chemical Relations of the Family. — The remaining elements of the third column of the periodic table, namely, **glucinum** or **beryllium** (Gl, or Be, at. wt. 9.1), **magnesium** (Mg, at. wt. 24.36), **zinc** (Zn, at. wt. 65.4), **cadmium** (Cd, at. wt. 112.4), and **mercury** (Hg, at. wt. 200.0), although all bivalent, do not form a coherent family. Glucinum and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water leaving the oxides, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, complex cations are not formed with ammonia, and the metals do not enter into complex anions. But glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal. Mercury is the only member of the group that forms two series of compounds. These are derived from the oxides HgO and Hg_2O. Mercury approaches the noble metals in the ease with which its oxide is decomposed by heating, and in the position of the free element in the electromotive series.

The vapor densities of zinc, cadmium, and mercury show the vapors of these three metals to be monatomic.

Glucinum Gl.

Glucinum (or beryllium) is bivalent in all its compounds. Its oxide and hydroxide are basic, and are also feebly acidic towards active bases (see Zinc hydroxide). The element derives its name from the sweet taste of its salts (Gk. γλυκύς, sweet).

Glucinum occurs in beryl, a metasilicate of glucinum and aluminium $Gl_3Al_2(SiO_3)_6$. Beryls, tinted green by the presence of a little silicate of chromium, are known as emeralds. The metal, obtained by electrolysis of the easily fusible double fluoride GlF_2, 2KF, burns when heated in the air. It displaces hydrogen from dilute acids, and when heated, from caustic potash: $Gl + 2KOH \rightarrow K_2GlO_2 + H_2$.

Magnesium Mg.

Chemical Relations of the Element. — Magnesium is bivalent in all its compounds. The oxide and hydroxide are basic exclusively. The element does not enter into complex cations or anions.

Occurrence. — Magnesium carbonate occurs alone as magnesite, and in a double salt with calcium carbonate $MgCO_3,CaCO_3$ as dolomite. The sulphate and chloride are found as hydrates and as constituents of double salts (see below) in the Stassfurt deposits. Olivine is the orthosilicate Mg_2SiO_4. Talc (soapstone) is an acid metasilicate $H_2Mg_3(SiO_3)_4$. Serpentine is a hydrated disilicate, $[Mg,Fe]_3,Si_2O_7,2H_2O$, as is also meerschaum. Asbestos is an anhydrous silicate. The element derives its name from Magnesia, a town in Asia Minor.

The Metal. — Magnesium is manufactured by electrolysis of dehydrated and fused carnallite $MgCl_2,KCl,6H_2O$. The iron crucible in which the material is melted forms the cathode, and a rod of carbon the anode. The metal is silver-white, and when heated can be pressed into wire and rolled into ribbon.

Chemically the metal is less active than are the metals of the alkaline earths. It slowly becomes coated with a layer of the carbonate. It displaces hydrogen easily from boiling water and, of course, from cold, dilute acids. Magnesium burns in air with a white light (p. 306, footnote). The ash contains the nitride Mg_3N_2, as well as the oxide.

Powdered magnesium is used in pyrotechny and, with potassium chlorate (10 : 17), in making flashlight powder for use in photography.

Magnesium Chloride $MgCl_2,6H_2O$. — This highly deliquescent salt occurs in salt deposits, alone, and as carnallite $MgCl_2$, KCl, $6H_2O$. The latter is an important source of potassium chloride (p. 362), and

almost all the magnesium chloride combined with it is thrown away. When the hexahydrate is heated, a part of the chloride is hydrolyzed, some magnesium oxide remaining, and some hydrogen chloride being given off. Sea-water cannot be used in ships' boilers because of the hydrochloric acid thus liberated by the magnesium chloride which the water contains. **Anhydrous** magnesium chloride $MgCl_2$ is obtained by heating the double chloride $MgCl_2,NH_4Cl,6H_2O$, for this salt can be dehydrated without hydrolysis of the chloride. The ammonium chloride is volatilized (p. 283).

The Oxide and Hydroxide. — **Magnesium oxide** MgO is made by heating the carbonate, and is known as "calcined magnesia." It is a white, highly infusible powder, and is used for lining electric furnaces and making crucibles. It combines slowly with water to form the **hydroxide** $Mg(OH)_2$.

The hydroxide is found in nature as brucite. It is also precipitated from solutions of magnesium salts by alkalies. It is very slightly soluble in water. The solution has a faint alkaline reaction.

Magnesium hydroxide is not precipitated by ammonium hydroxide when ammonium salts are present also. The ammonium salts, being highly ionized and giving a high concentration of ammonium-ion $NH_4^{\cdot}$, repress the ionization of the feebly ionized ammonium hydroxide, and so reduce the concentration of hydroxide-ion which it furnishes. With the ordinary concentration of $Mg^{\cdot\cdot}$, therefore, the amount of hydroxide-ion existing in presence of excess of a salt of ammonium is too small to bring the solubility product $[Mg^{\cdot\cdot}] \times [OH']^2$ up to the value required for precipitation (*cf.* p. 394). Conversely, magnesium hydroxide interacts with solutions of ammonium salts and passes into solution:

$$Mg(OH)_2(\text{solid}) \leftrightarrows \begin{matrix} Mg(OH)_2\ (\text{dslvd}) \leftrightarrows \\ 2NH_4Cl \qquad\qquad \leftrightarrows \end{matrix} \left.\begin{matrix} Mg^{\cdot\cdot} + 2OH' \\ 2Cl' + 2NH_4^{\cdot} \end{matrix}\right\} \leftrightarrows 2NH_4OH.$$

In presence of excess of ammonium chloride, the OH′ combines with $NH_4^{\cdot}$ to form molecular ammonium hydroxide, and the equilibria in the upper line are displaced forwards to generate a further supply of the former. With sufficiently great concentration of the ammonium chloride, all the magnesium hydroxide may thus dissolve. The whole case is analogous to the interaction of acids with insoluble salts (p. 397).

Other Salts of Magnesium. — The normal **carbonate** $MgCO_3$ is found in nature. Only hydrated *basic* carbonates are formed by precipitation, and their composition varies with the conditions. The carbonate manufactured in large amounts and sold as **magnesia alba** is approximately $Mg_4(OH)_2(CO_3)_3.3H_2O$.

The common **heptahydrate** of **magnesium sulphate** $MgSO_4,7H_2O$ crystallizes from cold water in rhombic prisms, and is called **Epsom salts**. The heptahydrate is efflorescent. The **monohydrate** which remains, and is found also in the salt layers as kieserite $MgSO_4,H_2O$, has a very low aqueous tension, and is not rapidly dehydrated except above 200°. Magnesium sulphate is used in the manufacture of sodium and potassium sulphates, and is employed also for "loading" cotton goods, and as a purgative.

The **sulphide** MgS may be formed by heating the metal with sulphur. It is insoluble in water, but is decomposed and gives, finally, hydrogen sulphide and magnesium hydroxide:

$$MgS + 2H_2O \rightleftarrows Mg(OH)_2 \downarrow + H_2S.$$

The only **phosphate** of importance is ammonium-magnesium orthophosphate $NH_4MgPO_4,6H_2O$, which appears as a crystalline precipitate when sodium phosphate and ammonium hydroxide (and chloride, p. 429) are mixed with a solution of a magnesium salt.

Analytical Reactions of Magnesium Compounds. — The magnesium ion is colorless and bivalent. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Potassium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

Zinc Zn.

Chemical Relations of the Element. — Zinc is bivalent in all its compounds. Of these there are two sets, — the more numerous and important one, in which zinc is the positive radical ($Zn.SO_4$, $Zn.Cl_2$, etc.), and a less numerous set, the zincates, in which zinc is in the negative radical ($Na_2.ZnO_2$, etc.). Both sets of salts are hydro-

lyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The element also enters into complex cations and anions. The salts are all poisonous.

Occurrence and Extraction from the Ores. — The chief sources of zinc are calamine or smithsonite $ZnCO_3$, zinc-blende (Ger. *blenden*, to dazzle) or sphalerite ZnS, franklinite $Zn(FeO_2)_2$, and zincite ZnO.

The ores are first converted into oxide, — the carbonate by ignition, and the sulphide by roasting. The sulphur dioxide is used to make sulphuric acid. A mixture of the oxide with coal is then distilled in earthenware retorts at 1300–1400°, the zinc condensing in earthenware receivers, while carbon monoxide burns at a small opening:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2,$$
$$ZnO + C \rightarrow CO + Zn.$$

At first zinc dust (a mixture of zinc and zinc oxide) collects in the receiver, and afterwards liquid zinc. The product, which is cast in blocks, is called spelter.

Properties and Uses of the Metal. — Zinc is a bluish-white crystalline metal. When cold it is brittle, but at 120–150° it can be rolled into sheets between heated rollers and then retains its pliability when cold. At 200–300° the metal becomes once more brittle, at 433° it melts, and at 920° it boils. The vapor at 1740° is monatomic.

The metal burns in air with a greenish flame, giving zinc oxide. In cold, moist air it is oxidized, and becomes covered with a firmly adhering layer of basic carbonate which protects it from further action. The metal displaces hydrogen from dilute acids. Zinc also attacks boiling alkalies, giving the soluble zincate (see below): $2KOH + Zn \rightarrow K_2ZnO_2 + H_2$.

Sheet zinc, in consequence of its lightness (sp. gr. 7), is used in preference to lead (sp. gr. 11.5) for roofs, gutters, and architectural ornaments. Galvanized iron is made by dipping cleaned sheet iron in molten zinc. The latter, being more active (p. 245), is rusted instead of the iron. Zinc is used also in batteries and for making alloys (p. 352). It mixes in all proportions with tin, copper, and antimony.

Zinc Chloride $ZnCl_2$.—This salt is usually manufactured by treating zinc with excess of hydrochloric acid, evaporating the solution to dryness, and fusing the residue. When hydrochloric acid is thus present, the chloride $ZnCl_2$ is obtained. Evaporation of the pure aqueous solution, which is acid in reaction, results in considerable hydrolysis and formation of much of the basic chloride Zn_2OCl_2:

$$ZnCl_2 + H_2O \rightleftarrows HCl + Zn(OH)Cl, \quad (1)$$
$$2Zn(OH)Cl \rightarrow Zn_2OCl_2 + H_2O. \quad (2)$$

The salt is used in solid form as a caustic and, by injection of a solution into wood (*e.g.*, railway sleepers), as a poison to prevent the growth of organisms which promote decay. In both cases the salt combines with albumins, forming solid products.

Zinc Oxide and Hydroxide and the Zincates.—The **oxide** ZnO is obtained as a white powder by burning zinc or by heating the precipitated basic carbonates. It turns yellow when heated, recovering its whiteness when cold, in the same way that mercuric oxide is brown whilst hot and bright red when cold. It is employed in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide.

The **hydroxide** $Zn(OH)_2$ appears as a white, flocculent solid when alkalies are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

$$Zn(OH)_2 + H_2SO_4 \leftrightarrows Zn.SO_4 + 2H_2O.$$

It also interacts with excess of the alkali employed to precipitate it, giving a soluble **zincate**, such as **potassium zincate** K_2ZnO_2:

$$H_2ZnO_2\uparrow + 2KOH \rightleftarrows K_2.ZnO_2 + 2H_2O.$$

Zinc hydroxide is ionized both as an acid and as a base:

$$2H^{\cdot} + ZnO_2'' \rightleftarrows Zn(OH)_2 \text{ (dslvd)} \rightleftarrows Zn^{\cdot\cdot} + 2OH'$$
$$\Updownarrow$$
$$Zn(OH)_2 \text{ (solid)}$$

The ionization as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrogen-ion; the hydroxyl ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the

other hand, the hydrogen-ion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left.

Zinc hydroxide interacts with ammonium hydroxide, giving the soluble **ammonia-zinc hydroxide** $Zn(NH_3)_4.(OH)_2$. The case is like those of copper (p. 414) and silver hydroxides (p. 420).

Compounds of zinc, when heated in the Bunsen flame with a salt of cobalt, gives a **zincate of cobalt** (Rinmann's green) $CoZnO_2$.

Other Salts of Zinc. — The normal **zinc carbonate** $ZnCO_3$ may be precipitated by means of sodium bicarbonate, but normal carbonate of sodium gives **basic carbonates**, such as $Zn_2(OH)_2CO_3$:

$$2ZnSO_4 + 2Na_2CO_3 + H_2O \rightarrow Zn_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2.$$

Zinc sulphate $ZnSO_4$ is formed when zinc-blende is roasted. It gives rhombic crystals of the **hydrate** $ZnSO_4, 7H_2O$. This, and the corresponding compounds of magnesium $MgSO_4,7H_2O$, of iron $FeSO_4$, $7H_2O$, and of other bivalent metals are known as **vitriols**. The zinc salt is **white vitriol**. It is used in cotton-printing and as an eye-wash (⅛ per cent solution). The sulphate gives double salts, such as **potassium-zinc sulphate** $ZnSO_4,K_2SO_4,6H_2O$ (*cf.* p. 231).

Zinc sulphide ZnS is more soluble in water than is sulphide of copper, and hence it interacts with excess of strong acids, and passes into solution. It is not soluble enough, however, to be much affected by weak acids like acetic acid (*cf.* p. 398). Zinc sulphide is thus capable of being precipitated when acetic acid is present, or when hydrogen sulphide is led into a solution of the acetate of zinc:

$$Zn(C_2H_3O_2)_2 + H_2S \rightleftarrows ZnS\downarrow + 2HC_2H_3O_2.$$

But when an active acid is present, or is formed, the sulphide is precipitated incompletely or not at all, the action being reversible:

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4.$$

There are thus two ways of obtaining the sulphide by precipitation. A soluble sulphide causes it to be thrown down completely, because no acid is liberated in the action:

$$ZnCl_2 + (NH_4)_2S \rightleftarrows ZnS\downarrow + 2NH_4Cl.$$

The other method is to add sodium acetate to the solution of the salt, and then lead in hydrogen sulphide. The acid which is liberated by

the action upon the salt interacts with the sodium acetate, giving a neutral salt of sodium and acetic acid, and the zinc sulphide is not affected by the latter (*cf.* p. 399).

Analytical Reactions of Zinc Salts. — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give Rinmann's green (p. 433).

Cadmium Cd.

Chemical Relations of the Element. — This element is bivalent in all its compounds. Its oxide and hydroxide are basic exclusively, and the salts are not hydrolyzed by water. It enters into complex compounds having the ions $Cd(NH_3)_4^{\cdot\cdot}$ and $Cd(CN)_4''$. Its resemblances to, and differences from zinc are especially noteworthy.

The Metal. — Aside from the rare mineral greenockite CdS, cadmium is found only in small amounts, as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first (b.-p. 770°). The metal is white, and is more malleable than zinc. It displaces hydrogen from dilute acids (*cf.* p. 245).

Compounds of Cadmium. — The **chloride** $CdCl_2,2H_2O$ is efflorescent and is not hydrolyzed during dehydration or in solution. Zinc chloride (p. 432) is deliquescent and is easily hydrolyzed.

The **hydroxide** $Cd(OH)_2$ is made by precipitation, and interacts with acids (as a basic hydroxide), but not at all with bases. It dissolves in ammonium hydroxide, however, forming $Cd(NH_3)_4.(OH)_2$. The **oxide** CdO is a brown powder, obtained by heating the hydroxide, carbonate, or nitrate, or by burning the metal.

The **sulphate** crystallizes from solution as $3CdSO_4,8H_2O$. Soluble carbonates throw down the **normal carbonate** of cadmium $CdCO_3$.

Hydrogen sulphide precipitates the yellow **sulphide** CdS even from acid solutions of the salts. The substance is used as a pigment. The

sulphide of cadmium, however, is less insoluble in water (*cf.* p. 397) than are the sulphides of copper and mercury, and therefore cannot be precipitated from a very strongly acid solution.

Analytical Reactions of Cadmium Compounds. — The cadmium ion $Cd^{\cdot\cdot}$ is bivalent and colorless. The yellow cadmium sulphide is precipitated by hydrogen sulphide, even from acid solutions of the salts. The white, insoluble hydroxide is not soluble in sodium hydroxide.

MERCURY Hg.

Chemical Relations of the Element. — Like copper, this element enters into two series of compounds, the mercurous Hg^{I} and the mercuric Hg^{II}. The mercurous halides, like the cuprous halides (and the argentic halides), are insoluble in water and are decomposed by light. Both of the oxides, Hg_2O and HgO, are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide, are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. No carbonate is known. Mercury enters into the anions of a number of complex salts, such as $HgCl_4''$, HgI_4'', $Hg(CN)_4''$, etc. It forms a class of mercury-ammonia compounds, like $Hg^{II}NH_2Cl$, all of which are insoluble.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 283), can all be volatilized completely. Mercury vapor and all mercury compounds are poisonous, the soluble ones more markedly so than the insoluble ones.

Occurrence and Isolation of the Metal. — Mercury occurs native and to a larger extent as red, crystalline cinnabar, mercuric sulphide HgS. The chief mines are in Spain, California, and Austria.

The liberation of the metal is easy, because, when roasted, the sulphide is decomposed, and the sulphur forms sulphur dioxide. The mercury does not unite with oxygen, for the oxide decomposes (p. 7) at 400–600°:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

In some places the ore is spread on perforated brick shelves in a vertical furnace, and the gases pass through tortuous flues in which the vapor of the metal condenses.

Physical Properties. — Mercury or quicksilver (N.L. *hydrargyrum*, from Gk. ὕδωρ, water, and ἄργυρος, silver) is a silver-white liquid. At − 39.5° it freezes, and at 357° it boils.

On account of its high specific gravity (13.6, at 0°) and low vapor tension, the metal is employed for filling barometers. Its uniform expansion favors its use in thermometers. The tendency to form amalgams, which it exhibits towards all the familiar metals with the exception of iron and platinum (the latter, however, is "wet" by it), is taken advantage of in various ways (*cf.* pp. 283, 423).

Chemical Properties. — When kept at a temperature near to its boiling-point, mercury combines slowly with oxygen. Mercury does not displace hydrogen from dilute acids (p. 245), but with oxidizing acids like nitric acid and hot concentrated sulphuric acid, the nitrates and sulphate (mercuric) are formed. With excess of mercury, mercurous nitrate, and with excess of the hot acid, mercuric nitrate, are produced. When mercury is divided into minute droplets, with relatively large surface, it is used in medicine ("blue pills"), and shows an activity which is entirely wanting in larger masses.

The Halides of Mercury. — **Mercurous chloride** $HgCl$ (**calomel**) is obtained as a white powder by precipitation from solutions of mercurous salts. It is made by subliming mercuric chloride with mercury:

$$HgCl_2 + Hg \rightarrow 2HgCl,$$

or more usually by subliming a mixture of mercuric sulphate, made as described above, with mercury and common salt. It is deposited on the cool part of the vessel as a fibrous crystalline mass, or, when the vapor is led into a large chamber, as a fine powder. It is slowly affected by light just as silver chloride is. Here, however, the chlorine which is released combines with another molecule of the salt to form mercuric chloride. The substance is used in medicine on account of its tendency to stimulate all organs producing secretions.

By direct union with chlorine, **mercuric chloride** $HgCl_2$ (**corrosive sublimate**) is formed. It is usually manufactured by subliming mercuric sulphate with common salt, and crystallizes in white, rhombic prisms. It melts at 265° and boils at 307°. The solubility at 20° is 7.4 : 100 Aq. The aqueous solution is slightly acid in reaction. The salt is easily reduced to mercurous chloride. When

excess of stannous chloride is added to the solution, the white precipitate of calomel, first formed, passes into a heavy gray precipitate of finely divided mercury:

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2HgCl,$$
$$2HgCl + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$

Corrosive sublimate, when taken internally, is extremely poisonous. A very dilute solution is used in surgery to destroy lower organisms and thus prevent infection of wounds. Mercuric chloride acts also as a preservative of zoölogical materials, forming insoluble compounds with albumins, and preventing decay. For the same reason, albumin (white of an egg) is given as an antidote in cases of sublimate poisoning.

Mercurous iodide HgI is formed by rubbing iodine with excess of mercury. It also appears as a greenish-yellow precipitate when potassium iodide is added to a solution of a mercurous salt. The compound decomposes spontaneously into mercury and mercuric iodide:

$$2HgI \rightleftarrows Hg + HgI_2.$$

Mercuric iodide HgI_2 is obtained by direct union of mercury with excess of iodine, or by addition of potassium iodide to a solution of a mercuric salt. It is a scarlet powder, insoluble in water, but soluble in alcohol and ether. It interacts with excess of potassium iodide, forming the soluble, colorless **potassium mercuri-iodide** $K_2.HgI_4$ with which many precipitants fail to give mercury compounds.

The Oxides. — When bases (excepting ammonium hydroxide, see p. 438) are added to solutions of mercurous salts, the greenish-black **mercurous oxide** Hg_2O is thrown down. The hydroxide is doubtless formed transitorily and then loses water (*cf.* Silver oxide, p. 420). Under the influence of light or gentle heat (100°), this oxide resolves itself into mercuric oxide and mercury.

Mercuric oxide HgO is formed as a red, crystalline powder, when mercury is heated in air near to 357°, but is usually made by decomposing the nitrate. Commercial specimens, incompletely decomposed, thus give some nitrogen peroxide when heated. It is formed also as a yellow powder by adding bases to solutions of mercuric salts.

Other Salts of Mercury. — **Mercurous nitrate** $HgNO_3,H_2O$ is formed by the action of cold, diluted nitric acid upon excess of mercury. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving a basic nitrate:

$$2HgNO_3 + H_2O \rightleftarrows HNO_3 + Hg_2(OH)NO_3 \downarrow.$$

On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:

$$Hg(NO_3)_2 + Hg \rightarrow 2HgNO_3 \quad \text{or} \quad Hg^{\cdot\cdot} + Hg \rightarrow 2Hg^{\cdot}.$$

Mercuric nitrate $Hg(NO_3)_2,8H_2O$ is produced by using excess of warm, concentrated nitric acid with mercury. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate $Hg_3(OH)_2O(NO_3)_2$. The hydrolysis is reversed by adding nitric acid.

Mercurous sulphide Hg_2S is formed by precipitation from mercurous salts, but decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide** HgS occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amorphous. By sublimation, in the course of which it dissociates, the black form gives the red, crystalline one.

The black and the red varieties do not interact with concentrated acids, or even with boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, still less soluble than is cupric sulphide (pp. 397–398). They are attacked, however, by *aqua regia*. The red form of the sulphide is used in making paint (**vermilion**).

Mercuric fulminate $Hg(ONC)_2$ is obtained as a white precipitate when mercury is treated with nitric acid, and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps.

Mercury-ammonia Compounds.—When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. Mercuric chloride gives $HgNH_2Cl$, commonly called "infusible white precipitate," and often **mercuri-ammonium chloride**:

$$HgCl_2 + 2NH_3 \rightarrow HgNH_2Cl + NH_4Cl.$$

Mercuric nitrate gives Hg_2NNO_3, sometimes called **dimercuri-ammonium nitrate**:

$$2Hg(NO_3)_2 + 4NH_3 \rightarrow Hg_2NNO_3 + 3NH_4NO_3.$$

The proper classification of these, and the other similar substances, is beyond the range of this book.

When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This appears to be a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate," $Hg + HgNH_2Cl$. To this reaction calomel owes its name (Gk. καλομέλας, beautiful black). Mercurous nitrate gives a black, insoluble mixture, $2Hg + Hg_2NNO_3$.

Analytical Reactions of Mercury Compounds. — The two ionic forms of the element, mercurous-ion $Hg^{\cdot}$ and mercuric-ion $Hg^{\cdot\cdot}$, are both colorless. Their chemical behavior is entirely different. Both give the black sulphide HgS, which is insoluble in acids and other solvents of mercury salts. Mercurous-ion gives the insoluble, white chloride, the black oxide, and a black mixture with ammonium hydroxide. Mercuric-ion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 437) is characteristic. With potassium iodide the two ions behave differently (p. 437). The more active metals displace mercury from all compounds. Copper is used as the displacing metal because the mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they give a sublimate of metallic mercury.

The Recognition of Cations in Qualitative Analysis.

"Wet-way" analysis consists in recognizing the various positive and negative ions present in a solution (p. 232). In discussing hydrogen sulphide (p. 254), it was stated that the sulphides might be divided into three classes according to their behavior towards water and acids. Now these differences furnish us with a basis for distinguishing the cations present in a solution.

The following plan, taken in conjunction with the statements in the context, shows how a single cation may be identified, and how, when several cations are present, a separation preparatory to identifi-

cation may be effected. What will be said applies only to the case of a *solution* containing salts like the chlorides, nitrates, or sulphates of one or more cations, and leaves the oxalates (p. 399), phosphates, cyanides, and some other salts, out of consideration.

Group 1. — Add, first, **hydrochloric acid**, to find out whether cations giving insoluble chlorides are present. Argentic, mercurous, and plumbic salts give the white **AgCl**, **HgCl**, and **$PbCl_2$**, respectively (*cf.* p. 422). Filtration eliminates the precipitate, if there is any.

Group 2. — A free, active acid being now present, **hydrogen sulphide** is led into the solution. The sulphides insoluble in active acids, namely, **HgS**, **CuS**, **PbS**, **Bi_2S_3**, **CdS**, **As_2S_3**, **Sb_2S_3**, **SnS**, **SnS_2** are therefore thrown down. The first four are black or brown, the next two and the last are yellow, and the remaining two are orange and brown respectively. A dark-colored substance will naturally obscure one of lighter color, if more than one is present. Filtration again eliminates the precipitate.

This group is easily subdivided. Any or all of the last four sulphides will pass into solution when warmed with yellow ammonium sulphide, for they give *soluble* complex sulphides (*q.v.*). The first five sulphides, or any of them, will be unaffected. On the other hand, these five sulphides, with the exception of HgS, will interact with hot nitric acid (p. 438). Other reactions are then used to distinguish between, or, if there is a mixture, to separate, the members of the sub-groups.

Group 3. — The solution (filtrate) is now neutralized with ammonium hydroxide, and **ammonium sulphide** is added. Some **ammonium chloride** is also used, to prevent the precipitation of magnesium hydroxide (p. 429), which, in any event, would be incomplete. The sulphides which are insoluble in water, and are not hydrolyzed by it, now appear. They are **FeS**, **CoS**, **NiS**, all black, **MnS,H_2O**, and **ZnS**, which are pink and white respectively. There are precipitated also the hydroxides of chromium and of aluminium, **$Cr(OH)_3$** and **$Al(OH)_3$**, because their sulphides are hydrolyzed by water.

Group 4. — After filtration, **ammonium carbonate** is added, and precipitates the remaining metals whose carbonates are insoluble, **$BaCO_3$**, **$SrCO_3$**, **$CaCO_3$**, with the exception of magnesium (p. 430).

By addition of **sodium phosphate** to a portion of the filtrate, magnesium, if present, now comes out in the form **NH_4MgPO_4**. There remain in solution only salts of **potassium**, **sodium**, and **ammonium**.

Since only ammonium compounds, and other substances which can be volatilized have been added, evaporation and ignition of the residue leaves the salts of the two metals. Salts of ammonium must be sought in a fresh sample by the usual test (p. 283).

Exercises. — 1. Why should we expect ammonium sulphide solution to precipitate magnesium hydroxide, and why does it not do so?

2. What volume of air is required to oxidize one formula-weight of zinc sulphide to ZnO and SO_2, and what volume of sulphur dioxide is produced? Is the gaseous product more, or less diluted with nitrogen than when pure sulphur is burned, and by how much?

3. Make equations showing, (*a*) the effect of heating zinc chloride with cobalt nitrate ($Co(NO_3)_2$) in the Bunsen flame (p. 433), (*b*) the action of hydrogen sulphide on sodium zincate, (*c*) the actions of concentrated nitric acid and of concentrated sulphuric acid on mercury.

4. What kind of salts might take the place of sodium acetate in the precipitation of zinc sulphide (p. 433, foot)? Give examples.

5. Why do none of the salts of the elements in this family give recognizable effects with the borax bead?

CHAPTER XXXVIII

ALUMINIUM AND THE METALS OF THE EARTHS

THE chief members of the family occupying the fourth column of the periodic table are: boron (B, at. wt. 11), aluminium (Al, at. wt. 27.1), gallium (Ga, at. wt. 70), indium (In, at. wt. 115), thallium (Tl, at. wt. 204.1), all on the right side of the column; and scandium (Sc, at. wt. 44.1), yttrium (Y, at. wt. 89), lanthanum (La, at. wt. 138.9), on the left side. These elements are all trivalent.

The Rare Elements of this Family.—The oxide and hydroxide of boron are acidic (p. 349). Those of aluminium ($Al(OH)_3$), gallium ($Ga(OH)_3$), indium ($In(OH)_3$), and thallium ($TlO.OH$) are basic, but behave also as acids towards strong bases.

Gallium and **indium** occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum.

Thallium is found in some specimens of pyrite and blende. It was discovered by Crookes, by means of the spectroscope, in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Gk. θαλλός, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium (*q.v.*). Thus, the salts of this series are more or less hydrolyzed by water. Univalent thallium recalls both sodium and silver. Thallous hydroxide ($TlOH$) is soluble, and gives a strongly alkaline solution. The chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium**, whose existence and properties were predicted by Mendelejeff (p. 276), is the best known. The metals of the **rare earths**, of which it is one, are found in rare minerals such as euxenite, gadolinite, orthite, and monazite, which occur in Sweden, Greenland, and the United States.

Cerium (Ce, at. wt. 140.25), **neodymium** (Nd, at. wt. 143.6), and **praseodymium** (Pr, at. wt. 140.5), occur along with **lanthanum** in cerite, a silicate of these four elements. These four are included amongst the metals of the rare earths. The compounds of many of these rare elements behave so much alike that separation is difficult. It is certain, however, that there are several with atomic weights near to that of lanthanum for which accommodation cannot easily be found in the periodic table. Ostwald has compared them to a group of minor planets such as in the solar system takes the place of one large planet.

ALUMINIUM.

The Chemical Relations of the Element. — Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 432), is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types $Na_3.AlO_3$ (sodium aluminate) and $Al_2.(SO_4)_3$. The salts of both series are more or less hydrolyzed by water, the former very conspicuously so. It is worth noting that the hydroxides of the trivalent metals, or metals in the trivalent condition, such as $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, are all distinctly less basic than are those of the bivalent metals such as $Zn(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$. Aluminium does not enter into complex anions or cations, and is too feebly base-forming to give salts like the carbonate or sulphite.

Occurrence. — Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The feldspars (such as $KAlSi_3O_8$), the micas (such as $KAlSiO_4$), and kaolin (clay $H_2Al_2(SiO_4)_2,H_2O$), are the commonest minerals containing it. Cryolite is a double fluoride $3NaF,AlF_3$. Various forms of the oxide and hydroxide are also found.

Preparation and Physical Properties. — The metal is now made on a large scale by electrolysis of the oxide (Al_2O_3) dissolved in a bath of molten cryolite. The operation is conducted in cells, the carbon linings of which form the cathodes. The anodes are rods of carbon which combine with the oxygen as it is liberated. The metal sinks to the bottom of the cell and is drawn off periodically, while fresh portions of the oxide are added from time to time. The current

(E.M.F. 5–6 volts) maintains the temperature of the molten materials, and causes the decomposition.

The metal melts at 600–700°, but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in hardness and tensile strength excells the other metals, with the exception of iron and copper. It has a silvery luster, and tarnishes very slightly, the firmly adhering film of oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (6–30 per cent) called **magnalium** has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium) is easily fusible, has a magnificent golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze. The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, and other articles requiring lightness and strength, as well as for the transmission of electricity. The powdered metal, mixed with oil, is used in making a silvery paint.

Chemical Properties. — The metal displaces hydrogen from hydrochloric acid very easily. It displaces hydrogen also from boiling solutions of the alkalies, forming aluminates:

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2.$$

In consequence of its very great affinity for oxygen, aluminium displaces all the metals, save magnesium, from their oxides. Thus, when a mixture of aluminium powder and ferric oxide is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$

The very high temperature (about 3000°) produced by the action is sufficient to melt both the iron (m.-p. 1550°) and the oxide of aluminium. The products, not being miscible, separate into two layers. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, **aluminothermy**. The sulphides, such as pyrite, are reduced with like vigor by aluminium.

Aluminium Chloride $AlCl_3$. — If the metal or the hydroxide is treated with hydrochloric acid, and the solution is allowed to evaporate, the **hydrated chloride** $AlCl_3,6H_2O$ is formed. When heated, this hydrate is completely hydrolyzed, hydrochloric acid is given off, and only the oxide remains. The **anhydrous chloride** $AlCl_3$ is made by passing dry chlorine over aluminium, or by heating the oxide with carbon in a stream of chlorine (*cf.* p. 344). Since it sublimes, as a white crystalline solid, without melting, when thus prepared it is vaporized and condenses in a cool part of the tube. It fumes when exposed to moist air on account of the hydrogen chloride produced by hydrolysis, and only with excess of hydrochloric acid does it give a clear solution free from basic salts.

Aluminium Hydroxide, the Aluminates and the Oxide. — When an alkali is added to a solution of a salt of aluminium, the **hydroxide** $Al(OH)_3$ is precipitated in gelatinous form. It loses water gradually when dried, forming no intermediate hydroxides, until Al_2O_3 remains. Natural forms of this substance are hydrargyllite $Al(OH)_3$ (= $Al_2O_3,3H_2O$), bauxite $Al_2O(OH)_4$ (= $Al_2O_3,2H_2O$), which always contains ferric oxide, and diaspore $AlO.OH$ (= Al_2O_3,H_2O).

Commercially, the hydroxide is made by heating bauxite with sodium carbonate, and extracting the sodium aluminate with water:

$$Al_2O(OH)_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O.$$

The hydroxide is then precipitated by passing carbon dioxide through the solution:

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3.$$

Aluminium hydroxide interacts both with acids and with bases, and is, therefore, like zinc hydroxide (p. 432), ionized both as a base and as an acid. It interacts only slightly with ammonium hydroxide, because this substance is too feebly basic, but, from the solution in the active alkalies, the **aluminates** $Na_3.AlO_3$, $Na.AlO_2$, and $K.AlO_2$, can be obtained in solid form. The aluminates are largely hydrolyzed by water:

$$NaAlO_2 + 2H_2O \rightleftarrows NaOH + Al(OH)_3.$$

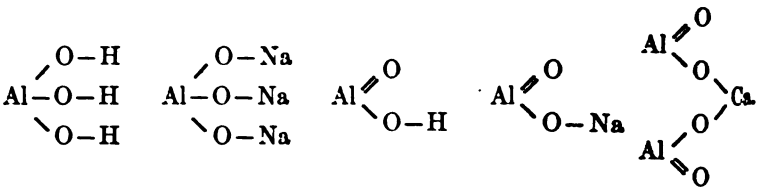
Sodium aluminate $NaAlO_2$ is used as a mordant (see below), on account of the ease with which the solution gives up aluminium

hydroxide when any material is present which can combine with the free portion of the hydroxide and so displace forward the above equilibrium.

When calcium chloride is added to a solution of sodium aluminate, the insoluble **calcium metaluminate** is deposited:

$$2NaAlO_2 + CaCl_2 \rightarrow Ca(AlO_2)_2 + 2NaCl.$$

The relations of these various substances are shown by the following formulæ:



A number of insoluble metaluminates are found in nature. They contain bivalent metals in place of the calcium in the last-named compound. Thus we have spinelle $Mg(AlO_2)_2$, and gahnite $Zn(AlO_2)_2$.

Aluminium oxide Al_2O_3 (**alumina**) is found in nature in pure form as corundum. This mineral is only one degree less hard than the diamond. Emery is a common variety, contaminated with ferric oxide, and is widely used as an abrasive. The ruby is pure aluminium oxide tinted by a trace of a compound of chromium, while the sapphire is the same material colored, possibly, with aluminate of cobalt. It is said, however, that the same tint is conferred upon colorless corundum by exposure to the influence of salts of radium.

Aluminium Sulphate: The Alums. — **Aluminium sulphate** $Al_2(SO_4)_3$, $18H_2O$ is prepared by treating either the hydroxide or pure clay (kaolin) with sulphuric acid. In the latter case the insoluble residue of silicic acid is removed by filtration:

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2H_2SiO_3 + 2H_2O.$$

The solution of the sulphate is acid in reaction. This compound is used as a mordant (see below) under the name of "concentrated alum." It is employed also in **sizing** cheaper grades of **paper**, an operation required to prevent the absorption and consequent spreading of the ink. For writing-paper, gelatine solution is employed. In making printing-papers, rosin soap (made by dissolv-

ing rosin in caustic soda) is mixed with the pulp, and aluminium sulphate is added. The rosin and aluminium hydroxide are precipitated in the pulp, perhaps in feeble combination, and pressing between hot rollers afterwards melts the former and gives a surface to the paper.

When sulphate of potassium is added to a strong solution of aluminium sulphate, octahedral crystals of potash alum (see below) are deposited. This is a double salt, and is one of a large class known as the **alums**. The alums have the general formula $M_2^{I}SO_4$, $M_2^{III}(SO_4)_3,24H_2O$, and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for M^{I} we may use K, NH_4, Rb, Cs, and Tl^{I}, and for M^{III}, Al, Fe^{III}, Cr^{III}, Mn^{III}, and Tl^{III}. All the alums crystallize in octahedra.

Potassium-aluminium sulphate $K_2SO_4,Al_2(SO_4)_3,24H_2O$, ordinary alum, is made from aluminium sulphate. It is also prepared by heating alunite, a basic alum found near Rome and in Hungary, and extracting the product with water. The alunite $KAl_3(OH)_6(SO_4)_2$ leaves an insoluble residue of the hydroxide, mixed with ferric oxide which is present as an impurity:

$$2KAl_3(OH)_6(SO_4)_2 \rightarrow K_2SO_4,Al_2(SO_4)_3 + 4Al(OH)_3.$$

The hydrated salt melts at 90°. An aqueous solution of this salt, or of sodium phosphate (p. 380), is used for fire-proofing draperies. The crystals deposited in the fabric melt easily, and the fused material protects the fibers from access of oxygen. When heated more strongly alum loses its water of hydration, together with some sulphur trioxide, and leaves a slightly basic, anhydrous salt known as **burnt alum**. A solution of alum dissolves a considerable amount of aluminium hydroxide, giving **neutral alum**, $K_2SO_4,Al_4(OH)_6(SO_4)_3$, a basic salt used as a mordant. The substance is usually prepared by adding sodium carbonate to the solution of alum as long as the aluminium hydroxide, formed locally, continues to redissolve.

Aluminium sulphide Al_2S_3 is most easily obtained by mixing pyrite with aluminium powder and igniting with magnesium ribbon (p. 444):

$$3FeS_2 + 4Al \rightarrow 2Al_2S_3 + 3Fe.$$

It forms a grayish-black solid, and is decomposed by water, like magnesium sulphide, giving the hydroxide and hydrogen sulphide.

Dyeing: Mordanting. — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do this in such a way that the dye is fast to (*i.e.*, is not removed or destroyed by) rubbing, and often, also, to washing with soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of hollow fibers of the composition of cellulose $(C_6H_{10}O_5)_x$. Wool is made of hollow fibers, also, and silk of rods, but the material is entirely different. It contains 17 per cent of nitrogen in the case of wool, and 20 per cent in the case of silk, and the nitrogen compounds of which the material is composed are much more active chemically than is cellulose, and combine incomparably more easily and firmly with the many kinds of organic compounds which are used as dyes. Hence, stains on wool and silk are much less often removable by washing than are those on cotton.

We have space to mention only **three kinds of dyes:**

1. **Insoluble colored bodies** which are formed by precipitation within the fibers and may be applied to any fabric, for their retention is due to mechanical and not to chemical causes. If cotton is boiled in a solution of lead acetate (or, better still, sodium plumbite, *q.v.*), and is then soaked in boiling potassium chromate solution, it is dyed a brilliant and permanent yellow. Lead chromate is the colored body:

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 \rightleftharpoons 2KC_2H_3O_2 + PbCrO_4\downarrow.$$

In indigo dyeing the fabric is saturated with a solution of indigo-white in caustic soda, and is then exposed to the air. Indigo-blue is formed by oxidation, and, being insoluble, is precipitated within the fibers:

$$2C_{16}H_{12}N_2O_2 + O_2 \rightarrow 2C_{16}H_{10}N_2O_2\downarrow + 2H_2O.$$

2. We have **direct** or **substantive dyes**, which are withdrawn from a solution by the goods which are being dyed, and confer upon the latter a depth of color depending on the strength of the solution and the affinity of the material for the dye. These dyes are fast on silk or wool, (for example, picric acid) but only a small minority of them are taken up by cotton or linen in such a way that they cannot be washed out. Congo red, $C_{32}H_{22}N_6S_2O_6Na_2$, is soluble in water, and is fast both on cotton and on wool.

3. The last class comprises the **mordant** or **adjective dyes.** They

work on the principle that the cloth is first impregnated with a substance capable of attaching itself both to the cloth and, subsequently, to the dye also, and is then immersed in the dye itself. Substances of this kind are tannic acid (for basic dyes) and colloidal hydroxides (for acid dyes) like those of aluminium, tin, iron, and chromium. They are called **mordants** (Lat. *mordere*, to bite). When aluminium hydroxide is to be used, the cloth is first treated with a hot solution of neutral alum, aluminium sulphate, or sodium aluminate, and thereby acquires, either by adsorption or feeble combination, a certain amount of the hydroxide (*cf.* p. 445). The fabric is then boiled in water with the dye. If, for example, alizarine (madder) is used, the cloth is dyed Turkey red. Alizarine is an orange-yellow, very slightly soluble acid of the composition $C_{14}H_8O_4$. Since the color is that of the *compound* of the dye with the mordant, different mordants give different colors, or shades of color, with the *same* dye.

Kaolin and Clay: Earthenware and Porcelain. — By the action of water and carbon dioxide upon granite and other rocks containing feldspar $KAlSi_3O_8$, the potash is slowly removed, and the compound changed largely into a hydrated orthosilicate $H_2Al_2(SiO_4)_2,H_2O$. When pure, it forms kaolin or china clay, a white, crumbly material. When washed away and redeposited, it usually acquires compounds of iron, and the carbonates of calcium and magnesium, becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

On account of its plasticity when moist, and its tendency to become hard, but not to melt, when heated strongly, clay is used in making **bricks, pottery,** and **porcelain.** The presence of calcium and magnesium carbonates makes the clay more fusible, that of silica less so. Iron compounds cause it to turn red during firing. For earthenware, glazing must be applied to make the vessels water-tight. This is often done by throwing salt into the kiln. The hot steam hydrolyzes the salt to sodium hydroxide and hydrochloric acid, and the former combines with the clay, giving a fusible silicate which fills the pores of the surface. For porcelain, very pure clay, free from iron, is employed, and it is mixed with feldspar and quartz. The feldspar melts and fills the pores so that a continuous, semi-transparent material results.

Analytical Reactions of Aluminium Compounds. — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide. The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt $Co(AlO_2)_2$.

Exercises. — 1. What are the differences between zinc and aluminium, and their corresponding compounds?

2. Construct equations showing, (*a*) the hydrolysis of aluminium sulphate (p. 446), (*b*) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (pp. 432, 445).

4. Why does zinc hydroxide, in spite of its feebleness as a base, dissolve in ammonium hydroxide, while aluminium hydroxide does not?

CHAPTER XXXIX

GERMANIUM, TIN, LEAD

THE metallic elements of the fifth column of the periodic table are **germanium** (Ge, at. wt. 72.5), **tin** (Sn, at. wt. 119), and **lead** (Pb, at. wt. 206.9). These are on the right side, while **titanium** (Ti, at. wt. 48.1), **zirconium** (Zr, at. wt. 90.6), **cerium** (Ce, at. wt. 140.25), and **thorium** (Th, at. wt. 232.5) occupy the left side.

The Chemical Relations of the Family. — All of these elements show a maximum valence of four. Germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. In this they resemble the potassium, calcium, and gallium families. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

GERMANIUM.

Germanium (p. 277) forms two oxides GeO and GeO_2 corresponding to those of carbon and of tin. **Germanious oxide** is not very definitely basic or acidic, and the sulphide is the only other well-defined compound of this set. **Germanic oxide** and hydroxide are acidic entirely. The resemblance to carbon is shown in the formation of an unstable compound with hydrogen, of **germanium chloroform** $GeHCl_3$ and of a volatile **chloride** $GeCl_4$ (b.-p. 87°).

TIN.

The Chemical Relations of the Element. — Tin is both bivalent and quadrivalent. Each of the oxides and hydroxides SnO and $Sn(OH)_2$, SnO_2 and $SnO(OH)_2$ (or $Sn(OH)_4$), is both basic and acidic,

so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable, although they are all more or less hydrolyzed by water, and sodium stannite $Na_2.SnO_2$ which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate Na_2SnO_3 is comparatively stable. The dioxide SnO_2 is an infusible solid, resembling silicon dioxide. Tin has a tendency to give complex acids and salts, like H_2SnCl_6, $(NH_4)_2.SnCl_6$, but these are ionized also to a small extent after the manner of double salts, giving ions of $Sn^{\cdot\cdot\cdot\cdot}$. Tin forms no salts with weak acids, like carbonic acid.

Occurrence and Extraction.—The chief ore of tin is tin-stone, or cassiterite SnO_2, which forms square-prismatic crystals whose dark color is due to the presence of iron compounds. It occurs in Cornwall and the East Indies. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace. The tin is afterwards remelted at a gentle heat, and the pure metal flows away from compounds of iron and arsenic. In 1900 the production was 4100 tons and 63,700 tons in England and in the East Indies, respectively. These quantities together constitute 83 per cent of the world's total output.

Physical and Chemical Properties.—Tin is a silver-white, crystalline metal of low tenacity but great malleability (tinfoil). Its specific gravity is 7.3, and its melting-point about 233°.

Tin-plate is made by dipping carefully cleaned sheets of mild steel into molten tin. Vessels of copper are also coated, internally, with tin, to prevent the formation of the basic carbonate (p. 411). For this purpose they are cleaned with ammonium chloride, sprinkled with rosin (to reduce the oxide), and heated to 230°. Molten tin is then spread on the surface with a piece of tow. Alloys of tin, such as bronze (p. 411), soft solder (50 per cent lead), pewter (25 per cent lead), and britannia metal (10 per cent antimony and some copper), are much used in the arts.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. With warm hydrochloric acid it gives stannous chloride $SnCl_2$ and hydrogen. Hot, concentrated sulphuric acid forms stannous sulphate $SnSO_4$ and sulphur dioxide (*cf.* p. 257). Nitric acid, when cold and dilute, interacts with it, giving stannous nitrate $Sn(NO_3)_2$, and a portion of the nitric acid is reduced to ammonia (*cf.* p. 297).

With concentrated nitric acid, stannic nitrate is formed, but most of this salt is hydrolyzed by the water at the high temperature of the action (*cf.* p. 438), and metastannic acid $(H_2SnO_3)_5$ (α-stannic acid) remains. The final result is shown by the equation (simplified):

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O.$$

Tin also displaces hydrogen from caustic alkalies, giving a metastannate, such as sodium metastannate Na_2SnO_3.

Chlorides of Tin. — **Stannous chloride** $SnCl_2$, $2H_2O$ is made by the interaction of tin and hydrochloric acid. When the crystals are heated, or when a strong aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride $Sn(OH)Cl$ is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 449).

Stannous chloride tends to pass into stannic chloride $SnCl_4$, and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 437) and of the noble metals, liberating the free metals. The action is of the form $Hg^{\cdot\cdot} + Sn^{\cdot\cdot} \rightarrow Hg + Sn^{\cdot\cdot\cdot\cdot}$. It also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in the acid solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:

$$6SnCl_2 + 2H_2O + O_2 \rightarrow 4Sn(OH)Cl + 2SnCl_4.$$

Powdered tin, if placed with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition.

When chlorine acts upon tin, or upon stannous chloride (either solid or dissolved), **stannic chloride** $SnCl_4$ is formed. The compound is a colorless liquid (b.-p. 114°) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It is almost completely hydrolyzed by water. The stannic acid which is formed is

not precipitated, however, but remains dissolved in colloidal (p. 96) form:

$$SnCl_4 + 4H_2O \rightleftarrows 4HCl + Sn(OH)_4.$$

The chloride, with small amounts of water, gives hydrates, of which $SnCl_4,5H_2O$, "oxymuriate of tin," is used as a mordant. Double (or perhaps complex) salts, such as ammonium-stannic chloride or "pink-salt" $(NH_4)_2SnCl_6$, (used as a mordant on cotton), are readily formed.

Stannic bromide $SnBr_4$ (b.-p. 201°) resembles stannic chloride.

α-Stannic Acid and its Salts. — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate of α-stannic acid is formed:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + H_2SnO_3 + H_2O.$$

The precipitate loses water gradually until the dioxide remains, and neither $Sn(OH)_4$ nor $SnO(OH)_2$ is obtainable as a definite compound. When stannic oxide is fused with caustic soda, **sodium metastannate**, or **α-stannate** $Na_2SnO_3,3H_2O$, is formed:

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$

This compound is used as a mordant under the name of "preparing salt." When its solution is acidified, the above mentioned α-stannic acid is formed by double decomposition. This α-stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

The α-stannates of the metals, aside from those of potassium and sodium, like the silicates and carbonates which they much resemble, are all insoluble in water, and may be made by double decomposition.

β-Stannic Acid, or Metastannic Acid. — The product of the action of nitric acid upon tin (p. 453) is a hydrated stannic oxide like the foregoing substance, but is not identical with it. It is not easily soluble in alkalies. By boiling it with caustic soda, however, and then extracting with pure water, a soluble **sodium β-stannate** $Na_2Sn_5O_{11}$, is obtained. β-stannic acid is also very slowly attacked by acids, and the chloride secured from it is not identical with the ordinary chloride. For these reasons it is supposed to be a hydrate of a polymer of stannic oxide $(SnO_2)_5,xH_2O$. When *fused* with caustic soda, it gives the same α-stannate as does the dioxide itself.

The Oxides of Tin. — When stannous oxalate is heated in absence of air, **stannous oxide** SnO remains: $SnC_2O_4 \rightarrow SnO + CO_2 + CO$. It is a black powder which burns in the air, giving the dioxide. The corresponding **hydroxide** $Sn_2O(OH)_2$ is formed by adding sodium carbonate to stannous chloride solution. It is a white powder, easily dehydrated, and interacts with alkalies to give soluble stannites, such as Na_2SnO_2. With acids, the hydroxide gives stannous salts.

Stannic oxide SnO_2 is found in nature (p. 452), and may be made in pure form by igniting β-stannic acid. When heated, it becomes yellow, but recovers its whiteness when cooled (*cf.* Zinc oxide, p. 432). Prepared at a low temperature, it interacts easily with acids, but after strong ignition, is affected by them very slowly.

The Sulphides of Tin. — **Stannous sulphide** SnS is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

Stannic sulphide SnS_2 is formed likewise by precipitation, and is yellow in color. Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide (or sodium sulphide), giving a soluble **complex sulphide**, namely, **ammonium sulphostannate**:

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2.SnS_3.$$

The corresponding **sodium sulphostannate** is easily crystallized in the form $Na_2SnS_3,2H_2O$. Stannous sulphide is not affected by soluble sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above mentioned sulphostannates:

$$SnS + (NH_4)_2S + S \rightarrow (NH_4)_2.SnS_3.$$

With acids the sulphostannates undergo double decomposition, but the free acid $H_2.SnS_3$ thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.

Analytical Reactions of Salts of Tin. — The two ionic forms of tin, $Sn^{\cdot\cdot}$, and $Sn^{\cdot\cdot\cdot\cdot}$, are both colorless. Their behavior is different. They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. These sulphides dissolve in yellow ammonium sulphide (above). The reducing power of stannous-ion $Sn^{\cdot\cdot}$ is very characteristic (p. 453). The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

LEAD.

The Chemical Relations of the Element. — Lead is both bivalent and quadrivalent. The oxides PbO and PbO_2, and the corresponding hydrated oxides, are all both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, but lead dioxide is a feeble one. Both are feebly acidic. The salts of bivalent lead, like $Pb(NO_3)_2$, commonly called the plumbic salts, are somewhat hydrolyzed by water, but less so than are those of tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites $Na_2.PbO_2$ and plumbates $Na_2.PbO_3$ are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent give up half of the negative radical readily, and are reduced to the "plumbic" condition. The metal displaces hydrogen with difficulty, and is easily displaced by zinc. Lead compounds are all poisonous, and the effects of repeated, very minute doses are cumulative,— resulting in "lead colic."

Occurrence and Metallurgy. — Commercial lead is almost all obtained from galena PbS, which crystallizes in cubes. This ore often contains considerable amounts of silver sulphide Ag_2S.

The sulphide of lead is first roasted until a sufficient proportion of it has been converted into the oxide and sulphate. The furnace-doors are then closed, and the temperature raised in order that these products may interact with the unchanged part of the sulphide:

$$PbS + 2PbO \rightarrow 3Pb + SO_2,$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2.$$

Another plan consists in heating galenite with scrap iron or iron ores and coal: $PbS + Fe \rightarrow Pb + FeS$. The molten ferrous sulphide rises to the top as a matte.

Physical and Chemical Properties. — Metallic lead is gray in color, very soft, and of small tensile strength. Its specific gravity is 11.4, and its melting-point 326°. While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets.

Type-metal contains 20–25 per cent of antimony (*q.v.*). In both cases greater hardness is secured by the addition of the foreign metal.

Lead oxidizes very superficially in the air. The suboxide Pb_2O is supposed to be first formed. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble, inclose the metal and protect the water from contamination with lead compounds. Pure rain-water, however, since it has no hardness, and contains oxygen in solution, gives the hydroxide $Pb(OH)_2$, which is noticeably soluble. When heated in the air, lead gives the monoxide PbO or minium Pb_3O_4, the latter at lower temperatures.

The metal displaces hydrogen from hydrochloric acid slowly. It is hardly affected by concentrated sulphuric acid (*cf.* p. 262). Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 298).

Chlorides and Iodide. — **Plumbic chloride** $PbCl_2$ is precipitated when a soluble chloride is added to a solution of a lead salt. It is slightly soluble in water (1.5 : 100) at 18°, and much more so at 100°.

Lead tetrachloride $PbCl_4$ is a solid at − 15°, and loses chlorine at the ordinary temperature. It is made by passing chlorine into plumbic chloride suspended in hydrochloric acid. The solution appears to contain H_2PbCl_6. When this is thrown into cold, concentrated sulphuric acid, an oil, $PbCl_4$, settles to the bottom. The oil fumes in the air, and closely resembles stannic chloride $SnCl_4$. With little water, it slowly deposits $PbCl_2$ and gives off chlorine. With much water it is quickly hydrolyzed, and lead dioxide is thrown down: $PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$.

The yellow **lead iodide** PbI_2 is formed by precipitation. It crystallizes in yellow scales from solution in hot water.

Oxides and Hydroxides. — There are five different oxides of lead, Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2. The **suboxide** Pb_2O is a dark-gray powder, formed by gently heating the oxalate. **Plumbic oxide**, or lead monoxide PbO, is made by cupellation (p. 418) of lead, and the solidified, crystalline mass of yellowish-red color is sold as "litharge." All the other oxides yield this one when they are heated above 600° in the air. Plumbic oxide takes up carbon

dioxide from the air, and therefore usually contains a basic carbonate. The oxide is used in glass-making and for preparing salts of lead.

Plumbic hydroxide $Pb(OH)_2$ is formed by precipitation. It gives up water in stages, the successive products being $Pb(OH)_2$, $Pb_2O(OH)_2$, $Pb_3O_2(OH)_2$. These substances are equivalent in composition to PbO,H_2O, $2PbO,H_2O$, and $3PbO,H_2O$ respectively. The hydroxide is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites**, like **sodium plumbite** $Na_2.PbO_2$.

Minium, or **red lead**, Pb_3O_4, gives off oxygen when heated:

$$2Pb_3O_4 \rightleftarrows 6PbO + O_2.$$

On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. It is therefore regarded as lead orthoplumbate (see below):

$$Pb_2.PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4.$$

The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable ($H_4PbO_4 \rightarrow PbO_2 + 2H_2O$), and the dioxide remains. Red lead is used in glass-making, and, when mixed with oil, gives a red paint.

Lead dioxide PbO_2 may be obtained as described above in the form of a brown powder. It is usually made by adding bleaching powder to an alkaline solution of plumbic hydroxide:

$$Na_2.PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2\downarrow.$$

In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. Lead dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and is not a peroxide in the restricted sense of the term (p. 212). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates**. The potassium salt $K_2PbO_3.3H_2O$ is analogous to the metastannate $K_2SnO_3,3H_2O$ (p. 454). A mixture

of calcium carbonate and lead monoxide absorbs oxygen when heated in a stream of air, and the yellowish-red calcium orthoplumbate is formed:

$$4CaCO_3 + 2PbO + O_2 \rightleftarrows 2Ca_2PbO_4 + 4CO_2.$$

The action is reversible, and is at the basis of Kassner's method of manufacturing oxygen from the air.

Other Salts of Lead. — **Lead nitrate** $Pb(NO_3)_2$ may be made by treating lead, lead monoxide, or lead carbonate with nitric acid. It forms white, anhydrous octahedra. The nitrate and acetate (see below) are the salts of lead which, because of their solubility (see Table), are most commonly used. On account of hydrolysis, the solution of the nitrate is acid in reaction.

Lead carbonate $PbCO_3$ is found in nature. It may be formed as a precipitate by adding a soluble bicarbonate to lead nitrate solution. With normal sodium carbonate, a basic carbonate $Pb_3(OH)_2(CO_3)_2$ is deposited. This basic salt is identical with **white lead**, which, on account of its superior opacity, has better covering power than zinc-white (p. 432) or permanent white (p. 405). The substance is manufactured in various ways, all of which involve the oxidation of the lead by the air, the formation of a basic acetate by the interaction of vinegar or acetic acid with the oxide, and the subsequent decomposition of the salt by carbon dioxide. The best quality is obtained by the Dutch method. In this, gratings of cast lead are placed above a shallow layer of vinegar in small pots. These pots are buried in manure, which by its decomposition furnishes the carbon dioxide and the necessary warmth. The gratings are gradually converted into a white mass of the basic carbonate. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent (*cf.* p. 54), since it is used over and over again.

Lead acetate $Pb(C_2H_3O_2)_2,3H_2O$ is made by the action of acetic acid on litharge. It is easily soluble in water, and, from the sweet taste of the solution, is named **sugar of lead** (used in medicine). The basic salt $Pb(OH)(C_2H_3O_2)$ is formed by boiling a solution of lead acetate with excess of litharge. Unlike most basic salts, this basic salt is soluble in water, and its solution has a faintly alkaline reaction.

Lead sulphate $PbSO_4$ occurs in nature as anglesite. Being insoluble in water, it is easily obtained by precipitation.

Natural **lead sulphide** PbS (galena) is black, and its crystals have a silvery luster. The precipitated salt is amorphous. It is more easily attacked by active acids than is mercuric sulphide (*cf.* p. 438).

Analytical Reactions of Lead Compounds. — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which dissolves in excess to form the plumbite. Potassium chromate or dichromate (*q.v.*) gives a yellow precipitate of **lead chromate** $PbCrO_4$, which is used as a pigment under the name of "chrome-yellow."

Titanium, Zirconium, Cerium, Thorium.

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

Titanium occurs in rutile $TiTiO_4$. Derived from it are a number of titanates of the form K_2TiO_3. **Zirconium** is found in zircon, the orthosilicate of zirconium $ZrSiO_4$. The oxide is used in making the incandescent substance in some forms of gas lamps.

Cerium occurs chiefly in cerite [Ce, La, Nd, Pd] SiO_4,H_2O (*cf.* p. 443).

Thorium is found in thorite $ThSiO_4$, but most of the supply comes from monazite sand. The nitrate $Th(NO_3)_4,6H_2O$ is used in making Welsbach incandescent mantles (*cf.* Flame, p. 338).

The **Nernst lamp** is an incandescent electric lighting arrangement in which a rod of the oxides of several of the rare metals takes the place of the common carbon filament. The peculiarity of this lamp is that preheating is required before the rod attains a temperature at which it will conduct the current. When this point has been once reached, the resistance enables the current to maintain the rod at the temperature of incandescence. For equal consumptions of electricity, this form of electric lamp gives a greater yield of light than does the ordinary, carbon-filament, incandescent bulb.

Exercises. — 1. In what order should you place the elements dealt with in this chapter, beginning with the least metallic, and ending with the most metallic (p. 353)?

2. Construct equations showing, (*a*) the interaction of tin and concentrated sulphuric acid, (*b*) of water and stannous chloride, (*c*) of oxygen and stannous chloride in acid solution, (*d*) the decomposition of lead oxalate (p. 457), (*e*) the interaction of lead monoxide and acetic acid, (*f*) and of lead monoxide and lead acetate.

3. To which class of ionic actions (pp. 243, 253, 412) do the reductions by stannous chloride and by tin (p. 453) belong?

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid?

5. How should you set about preparing, (*a*) lead oxalate (insoluble), (*b*) lead chlorate (soluble)?

CHAPTER XL

ARSENIC, ANTIMONY, BISMUTH

THIS family is very closely related to the elements phosphorus and nitrogen which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the chemistry of the corresponding compounds of phosphorus. For a general comparison of the elements **arsenic** (As, at. wt. 75), **antimony** (Sb, at. wt. 120.2) and **bismuth** (Bi, at. wt. 208) with each other and with the two already disposed of, see p. 471. It is sufficient here to say that arsenic is mainly an acid-forming element, and is therefore a non-metal, while antimony is both acid-forming and base-forming, and bismuth is base-forming. Each of the three elements gives two sets of compounds, in which it is trivalent, and quinquivalent, respectively. None of the free elements displaces hydrogen from dilute acids.

ARSENIC As.

The Chemical Relations of the Element. — Arsenic forms a compound with hydrogen AsH_3. It gives several halogen derivatives of the type AsX_3 which are completely hydrolyzed by water. Its oxides and hydroxides are acidic.

Sulphates, nitrates, carbonates, and other salts of arsenic are not formed. The complex sulphides (p. 455) are important.

Occurrence and Preparation. — Arsenic is found free in nature. It occurs also in combination with many metals, particularly in arsenical pyrites FeAsS. Two sulphides of arsenic, orpiment As_2S_3 and realgar As_2S_2, and an oxide As_2O_3, are less common.

The element is obtained either from the native material or by heating arsenical pyrites: $FeAsS \rightarrow FeS + As$. During the roasting of the sulphur ores of metals, arsenic trioxide is formed by the oxidation of the arsenic so frequently present, and collects as a dust in the flues.

Physical and Chemical Properties.—The free element is steel-gray in color, metallic in appearance, and crystalline in form. It is easily volatilized at 180°, and acquires a vapor pressure of 760 mm. long before the melting-point (480°, under high pressure) is reached. The density of the vapor measured at 644° gives 308.4 as the weight of the G.M.V. (22.4 liters at 0° and 760 mm.). The weight of arsenic combining with one chemical unit weight (35.45 g.) of chlorine, is 25 g. Three times this amount, or 75 g., is the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight (p. 134). Since 308.4 is equal approximately to 4×75 (= 300), the formula of the vapor of the simple substance at 644° is As_4. At 1700° the formula is As_2 (*cf.* p. 146).

The free element burns in the air, producing clouds of the solid trioxide As_2O_3. It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine water, and other powerful oxidizing agents (p. 194), it is oxidized in the same way as is phosphorus, and yields arsenic acid H_3AsO_4.

Arsine AsH_3. — This substance corresponds in composition to ammonia and phosphine, and some of the ways in which it may be formed are analogous to those used in the case of these substances. Thus, when arsenic and zinc are melted together in the proportions to form **zinc arsenide** Zn_3As_2, and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide, and arsine is evolved as a gas:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2.$$

Arsine (arsenuretted hydrogen) is formed also by the action of nascent hydrogen (*cf.* p. 302) upon *soluble* compounds of arsenic. When a solution of arsenious chloride $AsCl_3$ or arsenic acid is added to zinc and hydrochloric acid in a generating flask, arsine is formed:

$$AsCl_3 + 3H_2 \rightarrow AsH_3 + 3HCl.$$

Pure arsine may be secured by leading this mixture with hydrogen through a U-tube immersed in liquid air. The arsine (b.-p. − 40°) condenses as a colorless liquid.

Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide: $2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3$. The combustion of hydrogen containing arsine, generated as just described, gives the

same substances. Since arsine, when heated, is readily dissociated into its constituents (*cf.* p. 251), the vapor of free arsenic is present in the interior of the hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain. Even when only a trace of the compound of arsenic has been added to the materials in the generator, the stain which is produced is very conspicuous. This behavior thus furnishes us with the basis of an exceedingly delicate test — **Marsh's test** — for the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see Stibine).

Arsine is exceedingly poisonous, the breathing of small amounts producing fatal effects. It differs from ammonia more markedly than does phosphine, for it is not only without action on water or acids, but does not unite directly even with the halides of hydrogen.

Halides of Arsenic. — The halides include a liquid **trifluoride** AsF_3, a liquid trichloride, a solid **tribromide** $AsBr_3$, and a solid **triiodide** AsI_3.

The **trichloride** $AsCl_3$, which is prepared by passing chlorine gas into a vessel containing arsenic, is easily formed as the result of a vigorous action. It is a colorless liquid (b.-p. 130°). When mixed with water it is at once converted into the white, almost insoluble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 163), but the arsenious acid for the most part loses water and forms the insoluble anhydride:

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl,$$
$$2As(OH)_3 \rightleftarrows As_2O_3\downarrow + 3H_2O.$$

This action, however, differs markedly from the other in that it is reversible, and arsenic trioxide interacts with aqueous hydrochloric acid, giving a solution of arsenious chloride.

Oxides of Arsenic. — **Arsenic trioxide** As_2O_3 is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 462), and is known as "white arsenic" or simply "arsenic." It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in a glassy form in the upper part of the vessel.

When treated with water, the trioxide goes into solution to a very slight extent (0.3 : 100), forming arsenious acid, by reversal of the second of the actions given above. In boiling water the solubility is greater (11.5 : 100). When heated in a tube with carbon, this oxide is reduced, and the free element, being volatile, is deposited upon the cold part of the tube just above the flame. The trioxide is an active poison, since it gradually passes into solution, forming arsenious acid.

The **pentoxide** As_2O_5 is a white crystalline substance, formed by heating arsenic acid: $2H_3AsO_4 \rightarrow As_2O_5 + 3H_2O$. When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide. In consequence of this instability, it cannot be formed by direct union of oxygen with the trioxide, after the manner of phosphorus pentoxide.

Acids of Arsenic. — When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **orthoarsenic acid** H_3AsO_4 is produced. The substance, a deliquescent white solid, possesses a composition similar to that of orthophosphoric acid and, like the latter (p. 309), when heated loses water in progressive stages, furnishing intermediate acids — pyroarsenic acid and metarsenic acid — and finally the pentoxide. The relationship of the substances is shown by the formulæ:

$$H_3AsO_4 \rightarrow H_4As_2O_7 \rightarrow HAsO_3 \rightarrow As_2O_5.$$

These acids differ from the corresponding compounds of phosphorus in that upon solution in water they *immediately* pass back into the ortho-acid. With metaphosphoric acid, also, the final elimination of all the water by simple heating is impossible. The chocolate-brown **silver orthoarsenate** Ag_3AsO_4 and the white $MgNH_4AsO_4$, like the corresponding phosphates, are insoluble in water.

Arsenious acid H_3AsO_3, like sulphurous and carbonic acids, loses water, and yields the anhydride (arsenic trioxide) when the attempt is made to obtain it from the aqueous solution. The **potassium** and **sodium arsenites**, K_3AsO_3 and Na_3AsO_3, are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Paris green (p. 415) is an arsenite of copper. In cases of poisoning by white arsenic, freshly precipitated ferric

hydroxide (or the same compound in colloidal solution) or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble arsenates and arsenites.

Sulphides of Arsenic. — **Arsenic pentasulphide** As_2S_5 is obtained as a yellow powder by decomposition of the sulpharsenates (see below), and by leading hydrogen sulphide into a solution of arsenic acid in concentrated hydrochloric acid.

Arsenious sulphide As_2S_3 occurs in nature as orpiment, and was formerly used as a yellow pigment (*auripigmentum*). The word arsenic is derived from the Greek name for this mineral (ἀρσενικόν). It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride.

Realgar As_2S_2 is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrites and pyrite:

$$2FeAsS + 2FeS_2 \rightarrow 4FeS + As_2S_2\uparrow.$$

It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

Sulpharsenites and Sulpharsenates. — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of the sulphides of tin (p. 455), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3.AsS_3,$$
$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3.AsS_4.$$

Proustite (p. 417) is a natural sulpharsenite of silver.

These salts are decomposed by acids, and give the feebly ionized sulpharsenious or sulpharsenic acid:

$$(NH_4)_3.AsS_3 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_3 \rightarrow 3H_2S\uparrow + As_2S_3\downarrow$$
$$(NH_4)_3.AsS_4 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_4 \rightarrow 3H_2S\uparrow + As_2S_5\downarrow.$$

These sulpho-acids, however, at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates.

ANTIMONY Sb.

The Chemical Relations of the Element. — Antimony resembles arsenic in forming a hydride SbH_3 and halides of the forms SbX_3 and SbX_5. The latter are partially hydrolyzed by water with ease, but complete hydrolysis is difficult to accomplish with cold water. The oxide Sb_2O_3 is basic and also feebly acidic, and the oxide Sb_2O_5 is acidic. The compositions of the compounds are similar to those of the compounds of arsenic, but there are in addition salts, such as $Sb_2(SO_4)_3$, derived from the oxide Sb_2O_3. The element gives complex sulphides.

Occurrence and Preparation. — Antimony occurs free in nature. The black trisulphide Sb_2S_3, stibnite, is found in Hungary and Japan, and forms shining, prismatic crystals. Stibnite is roasted in the air in order to remove the sulphur, and the white oxide which remains is mixed with carbon and reduced by strong heat:

$$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2,$$
$$Sb_2O_4 + 4C \rightarrow 2Sb + 4CO.$$

Properties. — Antimony is a white, crystalline metal. It is brittle, and easily powdered. Its vapor at 1640° has the formula Sb_2, while at lower temperatures Sb_4 is present. It is used in making alloys such as type-metal, stereotype-metal, and britannia metal (*q.v.*). The alloys of antimony expand during solidification, and therefore give exceptionally sharp castings.

The element unites directly with the halogens. It does not rust, but when heated it burns in the air, forming the trioxide Sb_2O_3 or a higher oxide Sb_2O_4. When heated with nitric acid, it yields the trioxide and, with more difficulty, antimonic acid (H_3SbO_4).

Stibine SbH_3. — The hydride of antimony SbH_3 is formed by the action of zinc and hydrochloric acid on any soluble compound of antimony. By the action of dilute, cold hydrochloric acid on an alloy of antimony and magnesium (1 : 1), a mixture of hydrogen and stibine containing as much as 11.5 per cent (by volume) of the latter may be made. It is separated by cooling with liquid air (b.-p. − 18°, m.-p. − 91.5°). It is more easily dissociated than is arsine (p. 464), and forms a deposit of antimony when a porcelain vessel is held in the flame.

Antimony Halides. — The halides include the trichloride; the **pentachloride** $SbCl_5$, a liquid (b.-p. 140°); the **tribromide** $SbBr_3$, **triiodide** SbI_3, **trifluoride** SbF_3, and **pentafluoride** SbF_5.

Antimony trichloride $SbCl_3$ is made by direct union of chlorine and antimony. It forms large, soft crystals (m.-p. 73°), and used to be named "butter of antimony." When treated with little water, it forms a white, opaque, insoluble basic salt, antimony oxychloride:

$$SbCl_3 + H_2O \rightleftarrows SbOCl\downarrow + 2HCl.$$

With a large amount of water, a greater proportion of the chlorine is removed, and $Sb_4O_5Cl_2$ (= $2SbOCl,Sb_2O_3$) remains. With boiling water the oxide is finally formed. The action is not complete as long as hydrochloric acid is present. It may therefore be reversed, so that, on addition of hydrochloric acid to the mixture, a clear solution of the trichloride is re-formed. If the concentration of the acid is once more reduced by dilution with water, the oxychloride is again precipitated.

Oxides of Antimony. — The **trioxide** Sb_2O_3 is obtained by oxidizing antimony with nitric acid, or by combustion of antimony with a limited supply of oxygen. It is a white substance, insoluble in water. It is in the main a basic oxide, interacting with many acids to form salts of antimony. But it interacts also with alkalies, giving soluble **antimonites**. The **pentoxide** Sb_2O_5 is a yellow, amorphous substance, obtained by heating antimonic acid. It combines only with bases to form salts, and is therefore an acid-forming oxide exclusively. The **tetroxide** Sb_2O_4 is formed by heating antimony or the trioxide in excess of oxygen. It is neither acid- nor base-forming.

Salts of Antimony. — The **nitrate** $Sb(NO_3)_3$ and the **sulphate** $Sb_2(SO_4)_3$ are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts, such as $(SbO)_2SO_4$ (= $Sb_2O_2SO_4$), which, like SbOCl, are derived from the hydroxide SbO(OH). When the trioxide is heated with a solution of potassium bitartrate $KHC_4H_4O_6$, a basic salt $K(SbO)C_4H_4O_6$, known as **tartar-emetic**, is formed. This is a white, crystalline substance which is soluble in water and is used in medicine. The univalent group SbO^{I} is known as **antimonyl**, and the above mentioned basic compounds are often called antimonyl sulphate, etc.

Antimonic Acid. — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride with water, a white, insoluble substance of the approximate composition H_3SbO_4 is obtained. This substance interacts with caustic potash and passes into solution. But the salts which have been made are pyro- and metantimoniates. Thus, when antimony is fused with niter, **potassium metantimoniate** $KSbO_3$ is formed. When dissolved, this salt takes up water, giving a solution of the **acid potassium pyroantimoniate**:

$$2KSbO_3 + H_2O \rightarrow K_2H_2Sb_2O_7.$$

If this is added to a strong solution of a salt of sodium, an **acid sodium pyroantimoniate** is thrown down, $Na_2H_2Sb_2O_7$. This is almost the only insoluble salt of sodium.

Sulphides of Antimony. — The **trisulphide** Sb_2S_3 is found in nature as the black, crystalline stibnite. As precipitated from solutions of salts of antimony, the trisulphide is an orange-red powder, which, however, after melting, assumes the appearance of stibnite:

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$

Antimony trisulphide, like cadmium sulphide (p. 435), cannot be precipitated in presence of concentrated hydrochloric acid.

The **pentasulphide** Sb_2S_5 is obtained by the decomposition of sulphantimoniates (see below). In appearance it resembles the trisulphide and, when heated, decomposes into this substance and free sulphur.

The sulphides of antimony behave towards solutions of the alkali sulphides as do the sulphides of arsenic (p. 466). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable, soluble **ammonium sulphantimonite**

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3.$$

With the pentasulphide or with yellow ammonium sulphide the soluble **ammonium sulphantimoniate** is readily formed:

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3.SbS_4,$$
$$Sb_2S_3 + 3(NH_4)_2S + 2S \rightarrow 2(NH_4)_3.SbS_4.$$

The most familiar substance of this class is **Schlippe's salt** Na_3SbS_4, $9H_2O$. Pyrargyrite (p. 417) is a natural sulphantimonite.

When acids are added to solutions of sulphantimoniates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (see under Arsenic, p. 466).

Bismuth.

The Chemical Relations of the Element. — Bismuth forms no compound with hydrogen. Its compounds with the halogens are of the form BiX_3 and are hydrolyzed by water giving basic salts. The oxide Bi_2O_3 is basic, and the oxide Bi_2O_5 is not acidic. Bismuth gives a carbonate, nitrate, phosphate, and other salts, in which it acts as a trivalent element. It forms no soluble complex sulphides.

Occurrence and Properties. — This element is found free in nature, and also as trioxide Bi_2O_3 and trisulphide Bi_2S_3. It is a shining, brittle metal with a reddish tinge (m.-p. 270°). Mixtures of bismuth with other metals of low melting-point fuse at lower temperatures than do the separate metals. This is a corollary of the fact that a solution freezes at a lower temperature than does the pure solvent (p. 204). Thus, Wood's metal, containing bismuth (m.-p. 270°) 4 parts, lead (m.-p. 326°) 2 parts, tin (m.-p. 233°) 1 part, and cadmium (m.-p. 320°) 1 part, melts at 60.5°, considerably below the boiling-point of water. Similar alloys are used for safety plugs in steam-boilers and sprinklers.

Bismuth does not tarnish, but when heated strongly it burns to form the trioxide. With the halogens it forms a **fluoride** BiF_3, a **bromide** $BiBr_3$, and an **iodide** BiI_3. When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

Compounds of Bismuth. — In addition to the basic **trioxide** Bi_2O_3, which is a yellow powder obtained by direct oxidation of the metal or by ignition of the nitrate, three other oxides are known — BiO, Bi_2O_4, and Bi_2O_5. None of these, however, is either acid-forming or base-forming.

The salts of bismuth, when dissolved in water, give insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the **chloride** $BiCl_3.H_2O$ and the **nitrate** $Bi(NO_3)_3.5H_2O$, the actions taking place are:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl,$$
$$Bi(NO_3)_3 + 2H_2O \rightleftarrows Bi(OH)_2NO_3 + 2HNO_3.$$

The former of these products, when dried, loses a molecule of water, giving the **oxychloride** BiOCl. The **oxynitrate** $Bi(OH)_2NO_3$ is much used in medicine under the name of "subnitrate of bismuth."

The brownish-black **trisulphide** Bi_2S_3 may be obtained by direct union of the elements, or by precipitation with hydrogen sulphide. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

The Family as a Whole.

The elements themselves change progressively in physical properties as the atomic weight increases. Nitrogen is a gas which with sufficient cooling yields a white solid, phosphorus an almost white, or a red solid, and arsenic, antimony, and bismuth are metallic in appearance. The first combines directly with hydrogen, the next three give hydrides indirectly, and the last does not unite with hydrogen at all. The hydride of nitrogen combines with water to form a base, while the other hydrides show no such tendency. Ammonia unites with acids, including those of the halogens, to form salts; phosphine with the hydrogen halides only; the others do not combine with acids at all. As regards their metallic properties, in the chemical sense, nitrogen and phosphorus do not by themselves form positive ions, and furnish us therefore with no salts whatever. Arsenic gives a trivalent positive ion, which is found in solutions of the halides only. It forms no normal sulphates, nitrates, or other salts. Antimony and bismuth both give trivalent positive ions. The sulphates, nitrates, etc., of antimony, however, are readily decomposed by water with precipitation of the hydroxide. The salts of bismuth, on the other hand, do not readily give the pure hydroxide with water, although they are easily hydrolyzed to basic salts.

The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, and do not persist when any water is present, even when excess of the halogen acid is used. The halogen compounds of arsenic are completely hydrolyzed by cold water, but exist in solution in presence of excess of the acids. The halogen compounds of antimony and bismuth are incompletely hydrolyzed by cold water.

Each element gives a trioxide and a pentoxide. With nitrogen these are acid-forming, being the anhydrides of nitrous and nitric acids. With phosphorus the trioxide and the pentoxide are anhydrides of acids. With arsenic the trioxide is basic towards the halogen acids, and is the first example of a basic oxide which we encounter in this group. The pentoxide, however, is acid-forming. The trioxide of antimony is mainly base-forming, although it is feebly acid-forming also. The pentoxide is acid-forming. The trioxide of bismuth is base-forming exclusively, and the pentoxide has no derivatives.

These statements, which could easily be expanded, are sufficient to show that when the periodic law is borne in mind it furnishes valuable aid in systematizing the chemistry of a group like this.

Analytical Reactions of Arsenic, Antimony, and Bismuth. — The ions which are most frequently encountered are $As^{\cdots}$, $Sb^{\cdots}$, $Bi^{\cdots}$, AsO_4''', and AsO_3'''. The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. Marsh's test enables us to recognize the presence of traces of compounds of arsenic and antimony. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

Vanadium, Columbium, Tantalum.

Of these elements, **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium metavanadate** $NaVO_3$ is formed, and can be extracted with water. The element forms several **chlorides**, such as VCl_2, VCl_3, VCl_4, $VOCl_3$, and five **oxides**, V_2O, VO, V_2O_3, VO_2, and V_2O_5. The element has very feeble base-forming properties, and gives only a few unstable salts.

Columbium (or niobium) and **tantalum** possess feeble base-forming properties, their chief compounds being the columbates and tantalates.

Exercises. — 1. How do you account for the fact that the molecular weight of arsenic at 644° is not exactly 300, and why is 308.4 ÷ 4 not accepted as the atomic weight?

2. Formulate the series of changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed (*cf.* p. 251).

3. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid? Make the equation.

4. To what classes of chemical changes do the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide belong?

5. Construct equations showing the interaction of, (*a*) oxygen and arsenical pyrites, (*b*) chlorine-water and arsenic, (*c*) the dehydration of orthoarsenic acid, (*d*) potassium hydroxide and arsenic trioxide, (*e*) concentrated nitric acid and antimony, (*f*) potassium bitartrate and antimony trioxide, (*g*) acids and ammonium orthosulphantimoniate.

6. How should you set about making Schlippe's salt?

CHAPTER XLI

THE CHROMIUM FAMILY. RADIUM

THE chromium (Cr, at. wt. 52.1) family includes **molybdenum** (Mo, at. wt. 96), **tungsten** (W, at. wt. 184), and **uranium** (U, at. wt. 238.5), and occupies the seventh column of the periodic table along with the sulphur and selenium family.

The Chemical Relations of the Family. — The features which are common to the four elements are also those which affiliate them most closely with their neighbors on the right side of the column. They yield oxides of the forms CrO_3, MoO_3, WO_3, and UO_3, which, like SO_3, are acid anhydrides, and show the elements to be sexivalent. They give also acids of the form H_2XO_4, such as chromic acid H_2CrO_4. These acids correspond to sulphuric acid, and their salts, for example the chromates, resemble the sulphates.

Aside from the chromates, the first element forms also two basic hydroxides $Cr(OH)_2$ and $Cr(OH)_3$, from which the numerous chromous ($Cr^{\cdot\cdot}$) and chromic ($Cr^{\cdot\cdot\cdot}$) salts are derived. Uranium is base-forming, as well as acid-forming. Molybdenum and tungsten are not base-forming elements.

CHROMIUM Cr.

The Chemical Relations of the Element. — Chromium gives four classes of compounds, and most of them are colored substances (Gk. χρῶμα, color). The chromates are derived from chromic acid H_2CrO_4, which, however, is itself unstable, and leaves the anhydride CrO_3 when its solution is evaporated. The oxide and hydroxide in which the element is trivalent, namely Cr_2O_3 and $Cr(OH)_3$, are weakly basic and still more weakly acidic. Hence we have chromic salts such as $CrCl_3$ and $Cr_2(SO_4)_3$ which are somewhat hydrolyzed, but no carbonate, and no sulphide which is stable in water. The compounds in which the same hydroxide acts as an acid are the

chromites, and are derived from the less completely hydrated form of the oxide CrO(OH). Potassium chromite $K.CrO_2$ is more easily hydrolyzed, however, than is potassium zincate or potassium aluminate. Finally, the chromous salts such as $CrCl_2$ and $CrSO_4$ correspond to chromous hydroxide $Cr(OH)_2$ in which the element is bivalent. This hydroxide is more distinctly basic than is chromic hydroxide, and forms a carbonate and sulphide which can be precipitated in aqueous solution.

Occurrence and Isolation. — Chromium is found chiefly in ferrous chromite $Fe(CrO_2)_2$, which constitutes the mineral chromite, and in crocoisite $PbCrO_4$, which is chromate of lead. The metal may be made by reduction of the oxide with aluminium filings by Goldschmidt's method (p. 444).

Physical and Chemical Properties. — Chromium is steel-gray in color, very hard, and extremely infusible. It does not tarnish, but when heated it burns in oxygen, giving the green chromic oxide Cr_2O_3. It seems to exist in two states, an active and a passive one, the relations of which are still somewhat obscure. A fragment which has been made by the Goldschmidt method, or has been dipped in nitric acid, is passive, and does not displace hydrogen from hydrochloric acid. When, however, the specimen is warmed with this acid, it begins to interact, and thereafter behaves as if it lay between zinc and cadmium in the electromotive series. If left in the air, it slowly becomes inactive again.

Tin and iron with hydrochloric acid form stannous and ferrous chloride respectively, because the higher chlorides, if present, would be reduced by the active hydrogen (p. 302). Here, for the same reason, chromous chloride and not chromic chloride is formed:

$$Cr + 2HCl \rightarrow CrCl_2 + H_2 \quad \text{or} \quad Cr + 2H^{\cdot} \rightarrow Cr^{\cdot\cdot} + H_2.$$

Derivatives of Chromic Acid.

Potassium Chromate K_2CrO_4. — This and the sodium salt, or rather the corresponding dichromates (see below), are made directly from chromite, and form the starting-point in the preparation of the other compounds of chromium. The finely powdered mineral is mixed with potash and limestone, and roasted. The lime is employed

chiefly to keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$

The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO,Cr_2O_3) to that of chromic anhydride in the potassium chromate (K_2O,CrO_3). Thus, more insight is given into the nature of the action by the equation:

$$4(FeO,Cr_2O_3) + 8(K_2O,CO_2) + 7O_2 \rightarrow 2Fe_2O_3 + 8(K_2O,CrO_3) + 8CO_2.$$

The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

$$CaCrO_4 + K_2SO_4 \rightleftarrows CaSO_4 \downarrow + K_2CrO_4.$$

The whole of the potassium chromate goes into solution.

Potassium chromate is pale-yellow in color, gives anhydrous, rhombic crystals like those of potassium sulphate, and is very soluble in water (61 : 100 at 10°).

Sodium chromate $Na_2CrO_4,10H_2O$ is made by using sodium carbonate in the process just described.

The Dichromates. — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. The dry acid salt, when heated, loses water (p. 263), giving the pyrosulphate (or disulphate): $2KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O$, but the latter, when redissolved, returns to the condition of acid sulphate. Now, when an acid is added to a chromate we should expect the chromic acid H_2CrO_4, thus liberated, to interact, giving an acid chromate (say, $KHCrO_4$). No acid chromates are known, however, and instead of them, pyrochromates or dichromates are produced, with elimination of water. In other words, the second of the above actions is not appreciably reversible when chromates are in question:

$$\begin{array}{lll} K_2CrO_4 + H_2SO_4 & \rightarrow (H_2CrO_4) + K_2SO_4 & \\ K_2CrO_4\ (+\ H_2CrO_4) & \rightarrow K_2Cr_2O_7 + H_2O & \\ \hline 2K_2CrO_4 + H_2SO_4 & \rightarrow K_2Cr_2O_7 + H_2O + K_2SO_4 & (1) \end{array}$$

In terms of the ionic hypothesis, S_2O_7'' is unstable in water, and interacts with it, giving hydrogen-ion and sulphate-ion, while Cr_2O_7'' is stable in water and is formed from the interaction of hydrogen-ion and chromate-ion:

$$S_2O_7'' + H_2O \leftrightarrows 2H^{\cdot} + 2SO_4'',$$
$$Cr_2O_7'' + H_2O \leftrightarrows 2H^{\cdot} + 2CrO_4''. \qquad (2)$$

The dichromates of potassium and sodium are made by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 476). They crystallize when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition. For this reason the extract is always treated for dichromate.

Potassium dichromate $K_2Cr_2O_7$ (or K_2CrO_4,CrO_3) crystallizes in asymmetric tables of orange-red color. Its solubility in water is 8 : 100 at 10° and 12.5 : 100 at 20°. **Sodium dichromate** $Na_2Cr_2O_7$, $2H_2O$ forms red crystals also, and its solubility is 109 : 100 at 15°. This salt is now cheaper than potassium dichromate, and has largely displaced the latter for commercial purposes.

Chemical Properties of the Dichromates. — 1. When concentrated sulphuric acid is added to a strong solution of a dichromate (or chromate), **chromic anhydride** CrO_3 separates in red needles:

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CrO_3.$$

2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as SbOCl lacks hydroxyl, but is essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

The solution changes from red to yellow, and the chromate is obtained by evaporation. In this way the pure alkali chromates are made.

3. By addition of potassium dichromate to a solution of a salt of a metal whose chromate is insoluble, the chromate and not the dichromate is precipitated. This is in consequence of the fact that there is

always a little hydrogen-ion and CrO_4'' (equation (2), above) in the solution of the dichromate:

$$2Ba(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4\downarrow + 2KNO_3 + 2HNO_3.$$

Being essentially an acid salt, the dichromate produces a salt and an acid, as any acid salt would do. For example:

$$Ba(NO_3)_2 + KHSO_4 \rightleftarrows BaSO_4\downarrow + KNO_3 + HNO_3.$$

4. The dichromates of potassium and sodium melt when heated and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen. To make the equation, we note that the dichromate, for example $K_2Cr_2O_7$, consists of $K_2CrO_4 + CrO_3$, and the latter, if alone, will decompose thus: $2CrO_3 \rightarrow Cr_2O_3 + 3O$. Since the product must contain a multiple of O_2, the equation is:

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

5. With free acids the dichromates give powerful oxidizing mixtures, in consequence of their tendency to form chromic salts. Since the latter correspond to the oxide Cr_2O_3 and the former to CrO_3, the passage from the former to the latter must furnish 3O for every $2CrO_3$ transformed. In dilute solutions, unless a body capable of being oxidized is present, no actual decomposition, beyond the liberation of chromic acid * occurs. When concentrated hydrochloric acid is used, this acid itself suffers oxidation:

$$\begin{array}{l} K_2Cr_2O_7 + 8HCl \rightarrow 2KCl + 2CrCl_3 + 4H_2O\ (+\ 3O) \\ (3O) \quad + 6HCl \rightarrow 3H_2O + 3Cl_2 \\ \hline K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \end{array}$$

When sulphuric acid is employed, an oxidizable substance such as hydrogen sulphide (*cf.* p. 253), sulphurous acid, or alcohol must be present, if the dichromate is to be reduced:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O(+\ 3O) \quad (1)$$

$$(3O) + 3H_2SO_3 \rightarrow 3H_2SO_4 \quad (2)$$

or

$$(3O) + \underset{\text{[alcohol]}}{3C_2H_5OH} \rightarrow \underset{\text{[aldehyde]}}{3C_2H_4O}\uparrow + 3H_2O \quad (2')$$

In each case the usual summation of (1) and (2), with omission of the 3O gives the equation for the whole action. When (1) is dissected,

* Not shown as a distinct stage in the subsequent equations.

$K_2O,2CrO_3$ giving $Cr_2O_3,3SO_3 + 3O$ is found to be its essential content. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of aldehyde and in the dichromate battery.

6. When paper is coated with gelatine containing a soluble chromate or dichromate, and, after being dried, is exposed to light, chromic oxide is formed by reduction, and combines with the gelatine. This product will not swell up or dissolve in tepid water, as does pure gelatine. This action is used in many ways for purposes of artistic reproduction. Thus, if the gelatine mixture is made up with lampblack, and, after the coating has dried, is covered with a negative and exposed to light, the parts which were protected from illumination may afterwards be washed away, while the **carbon print** remains. The gelatine layer can be transferred to wood or copper before washing. When materials of different colors are substituted for the lampblack, prints of any desired tint may be made by the same process.

Insoluble Chromates. — A number of chromates, formed by precipitation with a solution of a soluble chromate or dichromate, are familiar. Thus, **lead chromate** $PbCrO_4$ is used as a yellow pigment. By treatment with lime-water it gives a basic salt of brilliant orange color, — **chrome-red** Pb_2OCrO_4. Salts of calcium give a yellow, hydrated **calcium chromate** $CaCrO_4$, $2HO_2$ analogous to gypsum, and, like it, perceptibly soluble in water (0.4 : 100 at 14°). **Barium chromate** $BaCrO_4$ is also yellow. Being a salt of a feeble acid, it interacts with active acids, and passes into solution. Like calcium oxalate (*cf.* p. 397), it is not soluble enough to be attacked by acetic acid. **Strontium chromate** $SrCrO_4$, however, is soluble in acetic acid. **Silver chromate** Ag_2CrO_4 is red, and interacts easily with acids. It will be observed that there is a close correspondence between the relative solubilities (see Table) of the chromates and the sulphates.

Chromic Anhydride CrO_3. — This oxide is made as described above (par. 1, p. 477), and is often called chromic acid. It is soluble in water, and combines with the latter to some extent, giving dichromic acid $H_2.Cr_2O_7$. In a solution acidified with an active acid it is much used as an oxidizing agent for organic substances. It interacts with acids in the same way as do the dichromates, giving chromic

salts and furnishing oxygen to the oxidizable body. When heated by itself, it loses oxygen readily, and yields the green chromic oxide: $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$.

Chromic and Chromous Compounds.

Chromic Chloride. — A hydrated chloride $CrCl_3$, $6H_2O$ is obtained by treating the hydroxide $Cr(OH)_3$ with hydrochloric acid and evaporating. When heated, this hydrate is hydrolyzed, and chromic oxide remains. The anhydrous chloride is formed by sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over a heated mixture of chromic oxide and carbon (*cf.* p. 344):

$$Cr_2O_3 + 3C + 3Cl_2 \rightarrow 2CrCl_3 + 3CO.$$

In this form the substance dissolves with extreme slowness, even in boiling water, but in presence of a trace of chromous chloride or stannous chloride it is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, bluish crystals of $CrCl_3$, $6H_2O$ are deposited. These give a bluish solution containing $Cr^{\cdot\cdot\cdot} + 3\,Cl'$, but boiling reproduces the green color. The green material is a basic salt of an exceptional nature. It has lost one unit of chlorine by hydrolysis, and one of the two others is not precipitated by nitrate of silver. The substance is supposed, therefore, to contain a complex cation and to have the formula CrClOH.Cl.

Chromic Hydroxide. — When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color, $Cr(OH)_3,2H_2O$, is thrown down. This loses water by stages, giving intermediate hydroxides such as $Cr(OH)_3$ and CrOOH, and finally Cr_2O_3. It interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form $KCrO_2$. When the solutions of the alkali chromites are boiled, the free chromic hydroxide, present in consequence of hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. Insoluble chromites, such as that of iron $Fe(CrO_2)_2$, are found in nature. Many of them, like $Zn(CrO_2)_2$ and $Mg(CrO_2)_2$, may be formed by fusing the oxide of the metal with chromic oxide; the action being similar to that used in making zincates (p. 433) and aluminates (p. 450).

Chromic Oxide Cr_2O_3. — This oxide is obtained as a green, infusible powder by heating the hydroxide; or, more readily, by heating dry ammonium dichromate; or by igniting potassium dichromate with sulphur and washing the potassium sulphate out of the residue:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3,$$
$$K_2Cr_2O_7 + S \rightarrow K_2SO_4 + Cr_2O_3.$$

Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is used for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an alkali nitrate or chlorate is added, the oxidation goes on more quickly. The alkaline solution of the chromites may be oxidized, for example by chlorine or bromine, and chromates are formed.

Chromic Sulphate $Cr_2(SO_4)_3$, $15H_2O$. — This salt crystallizes in reddish-violet crystals, and may be made by treating the hydroxide with sulphuric acid. It gives reddish-violet, octahedral crystals of **chrome-alum** (*cf.* p. 447), K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$, when mixed with potassium sulphate. This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 478), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet ($Cr^{\cdot\cdot\cdot}$), but when boiled becomes green. The green compound is formed by hydrolysis and is gummy and uncrystallizable. It even yields products which do not show the presence either of the $Cr^{\cdot\cdot\cdot}$ or the SO_4'' ion. It seems to be formed thus:

$$2Cr_2(SO_4)_3 + H_2O \rightleftarrows Cr_4O(SO_4)_6.SO_4 + H_2SO_4.$$

The green materials revert slowly to the violet ones by reversal of the above action when the solution remains in the cold, and so crystals of the sulphate or of the alum are obtainable from the green solutions.

Chromous Compounds. — By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride** $CrCl_2$ is formed. The anhydrous salt is

colorless, and its solution is blue ($Cr^{\cdot\cdot}$). Like stannous chloride, it is very easily oxidized by the air, a solution of it containing excess of hydrochloric acid being used in the laboratory to absorb oxygen:

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O.$$

Chromous hydroxide $Cr(OH)_2$ is obtained as a yellow precipitate when alkalies are added to the chloride. With sulphuric acid it gives **chromous sulphate** $CrSO_4, 7H_2O$, which is one of the vitriols (p. 433).

Analytical Reactions of Chromium Compounds. — The chromic salts give the bluish-violet chromic-ion $Cr^{\cdot\cdot\cdot}$, or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions CrO_4'' and Cr_2O_7'', which are yellow and red respectively. From chromic salts, alkalies and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (*cf.* p. 417), both in color and in being unreducible.

Molybdenum, Tungsten, Uranium.

Molybdenum. — This element is found chiefly in wulfenite $PbMoO_4$ and molybdenite MoS_2. The latter resembles black lead (graphite), and its appearance suggested the name of the element (Gk. μολύβδαινα, lead). The molybdenite is converted by roasting into **molybdic anhydride** MoO_3. When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate** $(NH_4)_2MoO_4$, or **sodium molybdate** $Na_2MoO_4, 10H_2O$ is obtained. The **metal** itself is liberated by reducing the oxide or chloride with hydrogen. When pure it resembles wrought iron and, like iron (*q.v.*), takes up carbon and shows the phenomena of tempering. The **oxides** [MoO ?], Mo_2O_3, MoO_2, and MoO_3 are known, but the lower oxides are not

basic. The **chlorides** Mo_3Cl_6, $MoCl_3$, $MoCl_4$, and $MoCl_5$ have been made. The chief use of molybdenum compounds in the laboratory is in **testing for** and estimating **phosphoric acid.** When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a **phosphomolybdate of ammonium** $(NH_4)_3PO_4,11MoO_3,6H_2O$ is formed. The compound is soluble in excess of phosphoric acid and in alkalies, but not in dilute mineral acids.

Tungsten. — The minerals scheelite $CaWO_4$ and wolfram $FeWO_4$ are tungstates of calcium and iron respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate** $Na_2WO_4,2H_2O$ is secured. It is used as a mordant and for rendering muslin fire-proof. Acids precipitate **tungstic acid** H_2WO_4, H_2O from solutions of this salt. The element gives the **oxides** WO_2 and WO_3, the latter being formed by ignition of tungstic acid. The **chlorides** WCl_2, WCl_4, WCl_5, and WCl_6 are known, the last being formed directly, and the others by reduction. A hard variety of steel contains 5 per cent of tungsten.

Uranium. — This element is found chiefly in pitchblende, which contains the oxide U_3O_8 along with smaller amounts of many other elements. By roasting the ore with carbonate and nitrate of sodium, and extracting with water, an impure solution of **sodium uranate** $NaUO_4$ is obtained. Acids precipitate the insoluble, yellow **diuranate** $Na_2U_2O_7$, $6H_2O$. This salt is used in making **uranium glass,** which shows a yellowish-green fluorescence. The property is due to the fact that the wave-length of part of the invisible, ultra-violet rays of the sunlight are shortened, and a greenish light is therefore in excess. The **oxides** are UO_2 a basic oxide, U_2O_3, U_3O_8 the most stable oxide, UO_3 uranic anhydride, and UO_4 a peroxide.

When the oxide UO_2 is treated with acids, it gives uranous salts such as **uranous sulphate** $U(SO_4)_2$, $4H_2O$. Uranic anhydride and uranic acid interact with acids, giving basic salts, such as UO_2SO_4, $3\frac{1}{2}H_2O$, and $UO_2(NO_3)_2$, $6H_2O$, which are named **uranyl sulphate, uranyl nitrate,** and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable **uranyl sulphide** UO_2S from their solutions.

Radium.

The Discovery of the Element. * — It was Becquerel who first noticed (1896) that all compounds of uranium give out a radiation capable of slowly affecting a photographic plate covered with black, light-proof paper. These rays have a second, equally remarkable property. A well-insulated, electrically charged body, such as an electroscope, will retain its charge for a long time. Yet a few tenths of a gram of any uranium compound, brought within 3 or 4 cm. of the charged body, render the air a conductor, and the charge is quickly lost. The air is said to be "ionized." For the quantitative measurement of radio-activity, or the rate of production of Becquerel rays, we simply have to compare the times required for the discharge of an electroscope by different specimens of radioactive matter.

The radio-activity of every pure uranium compound is proportional to its uranium content. The *ores* are, however, relatively four times as active. This fact led M. and Mme. Curie to the discovery that the pitchblende residues, from which practically all of the uranium had been extracted, were nevertheless quite active. About a ton of the very complex residues having been separated laboriously into the constituents, it was found that a large part of the radioactivity remained with the chloride of barium. From this barium chloride, a product free from barium, and three million times as active as uranium, was finally secured. The nature of the spectrum and the chemical relations of the element, now named **radium**, placed it with the metals of the alkaline earths. The ratio by weight of chlorine to radium in the compound is 35.45 : 113.25, so that, on the assumption that the element is bivalent, its atomic weight is 326.5. With this value it occupies a place formerly vacant in the periodic table.

Properties of Radium Compounds. — Radium has not been isolated, and the **chloride** $RaCl_2$ and **bromide** $RaBr_2$ are usually employed. The extraordinary photo-activity and ionizing power of the compounds have been mentioned above. The most remarkable property of the salts, however, is their constant evolution of heat in relatively enormous quantities. One gram of the element,

* I am indebted to my colleague Professor H. N. McCoy for the material of which the following is a slightly condensed version.

in combination, evolves over 100 cal. per hour, and it is estimated that the total amount of heat spontaneously produced by 1 g. would be nearly 10^{10} cal. To produce the same amount of heat by combustion, no less than 300 kg. of hydrogen would have to be burned. The heating effect is explained by the hypothesis that the rays emitted by the radium consist of minute particles whose impacts produce the heat. To explain all the properties we are compelled to suppose that there are two kinds of these particles, electrons, or corpuscles, namely those which produce the ionization (α-particles) and those which produce the photographic effects (β-particles). The former bear positive charges and have twice the mass of a hydrogen atom. The latter bear negative charges and have only about 1/1000th of the mass of a hydrogen atom.

The Decay of an Element. — The radium in disintegrating and giving off these particles, produces a new radio-active, gaseous body, the **radium emanation.** This is not permanent, and loses half its activity in about four days. In doing so it produces a series of new radio-active substances. The members of the series with their times of decay to half value, are as follows (Rutherford):

U	→	U-X	→	Ionium	→	Ra	→	Em	→	A	→
5×10^{9}yrs.		22 days		?		2000 yrs.		3.8 days		3 min.	
B	→	C	→	D	→	E	→	F	→	G	
26 min.		19 min.		40 yrs.		6 days		45 days		140 days	

Radium thus loses its activity. To account for its presence in the ore, we must, therefore, suppose that it is being continuously produced from some source. This source must be uranium, for every known uranium ore contains radium (McCoy) and radium emanation (Boltwood) in amounts proportional to the uranium content. Furthermore, the radium emanation is slowly re-formed in a uranium compound previously freed from radium (Soddy).

It has been found (Ramsay and Soddy) that helium (p. 290) is one of the decomposition products of the radium emanation, and, more recently, that cupric nitrate solution, when inclosed with some of the radium emanation, acquires a small proportion of lithium nitrate (Ramsay and Cameron). The fact that all uranium-radium minerals which contain copper, contain also lithium (McCoy), confirms this observation of the degradation of copper to that member

of the same family possessing the lowest atomic weight. The phenomena of radio-active substances lead undeniably to the startling conclusion that *some, if not all, of the elements are capable of spontaneous decomposition.*

Exercises. — 1. Construct equations, showing the interactions of: (*a*) chromic oxide and aluminium, (*b*) strontium nitrate and potassium dichromate in solution, (*c*) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (*d*) chlorine and potassium chromite in excess of alkali (what is the actual oxidizing agent?).

2. What volume of oxygen at 0° and 760 mm., (*a*) is obtainable from one formula-weight of potassium dichromate (par. 4, p. 478), (*b*) is required to oxidize one formula-weight of chromous chloride?

3. To what classes of actions should you assign the three methods of making chromic oxide (p. 481)?

CHAPTER XLII

MANGANESE

The Chemical Relations of the Element. — Manganese stands, at present, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens. It is never univalent, as the halogens are, but its heptoxide Mn_2O_7 and the corresponding acid, permanganic acid $HMnO_4$, are in many ways closely related to the heptoxide of chlorine and perchloric acid $HClO_4$. Of the lower oxides of manganese, MnO is basic, and Mn_2O_3 feebly basic. MnO_2 is feebly acidic, MnO_3 more strongly so, and permanganic acid (from Mn_2O_7) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and the acidic oxides (with the possible exception of Mn_2O_3) are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and the most important.

1. **Manganous compounds**, MnO, $Mn(OH)_2$, $MnSO_4$, etc. These compounds resemble those of the magnesium family (and those of $Fe^{\cdot\cdot}$). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little hydrolysis of the halides. The salts are pale-pink in color.

2. **Manganic compounds**, Mn_2O_3, $Mn(OH)_3$, $Mn_2(SO_4)_3$, $[MnCl_3]$. The salts resemble the chromic and aluminium salts in behavior, but are even less stable than those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites**, MnO_2, H_2MnO_3, $CaMnO_3$. The alkali manganites are strongly hydrolyzed, like the plumbates and the stannates.

4. **Manganates**, MnO_3, H_2MnO_4, K_2MnO_4. The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid in that when it decomposes it

yields a higher acid ($HMnO_4$) and a lower oxide (MnO_2). The salts are green in color.

5. **Permanganates**, Mn_2O_7, $HMnO_4$(hydrated), $KMnO_4$. The salts resemble the perchlorates, and are not hydrolyzed by water. They are reddish-purple in color.

It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed.

Occurrence: the Metal. — The chief ore is the dioxide, pyrolusite MnO_2, which always contains compounds of iron. Other manganese minerals are: braunite Mn_2O_3; the hydrated form, manganite $MnO(OH)$; hausmannite Mn_3O_4; and manganese spar $MnCO_3$. The metal is most easily made by reducing one of the oxides with aluminium by Goldschmidt's method.

The metal manganese has a grayish luster faintly tinged with red. It rusts in moist air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as ferro-manganese (20–80 per cent manganese), are used in the arts.

Oxides. — **Manganous oxide** MnO is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite** Mn_3O_4 is red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (*cf.* p. 458). **Manganic oxide** Mn_2O_3 is brownish-black, and is formed by heating any of the oxides in oxygen.

Manganese dioxide MnO_2 is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. The hydrated forms of the oxide are produced by precipitation, as by adding a hypochlorite or hypobromite to manganous hydroxide suspended in water. Manganese dioxide is not a peroxide in the restricted sense (*cf.* p. 212). That is to say, it does not contain the radical (O_2) and, therefore, does not give hydrogen peroxide. Its reaction formula is $Mn(O)_2$ not $Mn(O_2)$ and in double decompositions it yields only water $H_2(O)$. It is used for manufacturing chlorine, although electrolytic processes are now driving it out of this field. In glass-making (*q.v.*), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric

compound. The amethyst color of the manganic silicate which is formed tends to neutralize this yellow.

Manganese trioxide MnO_3 is a red, unstable powder. **Manganese heptoxide** Mn_2O_7 is a brownish-green oil (see below).

When any of these oxides is heated with an *acid*, a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical. In this action the oxides containing more oxygen than does MnO give off oxygen, or oxidize the acid (*cf.* p. 112). When the oxides are heated with *bases*, in the presence of air, manganates are always formed. In this case, with oxides containing a smaller proportion of oxygen than MnO_3, oxygen is taken from the air.

Manganous Compounds.—The manganous salts are formed by the action of acids upon the carbonate or any of the oxides. Thus the **chloride** $MnCl_2,4H_2O$ is obtained in pale-pink crystals from a solution made by treating the dioxide with hydrochloric acid and driving off the chlorine liberated by oxidation (p. 112). The **hydroxide** $Mn(OH)_2$ is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated in their presence on account of the formation of molecular ammonium hydroxide and the suppression of hydroxide-ion (*cf.* magnesium hydroxide, p. 429). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide MnO(OH).

Manganous sulphate gives pink crystals of a hydrate. Below 6° the solution deposits $MnSO_4,7H_2O$, which is a vitriol (p. 433). Between 7° and 20° the product is $MnSO_4,5H_2O$, asymmetric and resembling $CuSO_4,5H_2O$. Above 25° monosymmetric prisms of $MnSO_4,4H_2O$ are obtained. These hydrates have different aqueous tensions and may be formed from one another by lowering or raising the pressure of water vapor around the substance (p. 83).

Manganous carbonate $MnCO_3$ is a white powder formed by precipitation. The **sulphide** MnS is obtained as a green powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, **hydrated manganous sulphide** MnS, H_2O or MnSH(OH) is more familiar and is precipitated by ammonium sulphide from manganous salts. It interacts with mineral acids and even with acetic acid, so that it cannot be precipitated by hydrogen sulphide (*cf.* p. 254).

The manganous salts of weak acids, such as the carbonate and sulphide, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. As we have seen, manganous hydroxide is similarly oxidized and these salts are precisely the ones which should furnish the hydroxide by hydrolysis. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

Manganic Compounds. — The base of this set of compounds, **manganic hydroxide** $Mn(OH)_3$, is slowly deposited by the action of the air on an ammoniacal solution of a manganous salt in salts of ammonium. **Manganic chloride** $MnCl_3$ is present in the liquid obtained by the action of hydrochloric acid upon manganese dioxide (*cf.* p. 111), but loses chlorine very readily.

Manganites. — Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from $H_2MnO_3(=H_2O, MnO_2)$ or $H_4MnO_4(=2H_2O.MnO_2)$ are not formed. The products are complex, as $K_2Mn_3O_{11}$. Some less complex manganites are formed in the **Weldon process** for utilizing the manganous chloride obtained in manufacturing chlorine. The liquor is mixed with slaked lime, and air is blown through the mass of calcium and manganous hydroxides which is thus obtained. Black manganites of calcium, such as $CaMnO_3(=CaO,MnO_2)$ and $CaMn_2O_5(CaO, 2MnO_2)$ are thus formed:

$$Ca(OH)_2 + 2Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O,$$

and when afterwards treated with hydrochloric acid they behave like mixtures of manganese dioxide and calcium oxide.

Manganates. — When one of the oxides of manganese is fused with potassium carbonate and potassium nitrate a green mass is obtained. The green aqueous extract deposits **potassium manganate** K_2MnO_4 in rhombic crystals, which are of the same form as those of potassium sulphate, and are almost black:

$$K_2CO_3 + MnO_2 + O \rightarrow K_2MnO_4 + CO_2.$$

The acid H_2MnO_4 is itself unknown. The potassium salt remains unchanged in solution only in presence of free alkali. When the concentration of the hydroxide-ion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is decomposed according to the following equation:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2.$$

That is, a precipitate of manganese dioxide, and a solution of potassium permanganate are obtained. In terms of the ions the equation is simpler:

$$3MnO_4'' + 2H^{\cdot} \rightarrow 2OH' + 2MnO_4' + MnO_2.$$

Permanganates. — **Potassium permanganate** $KMnO_4$ is made by decomposition of the manganate as shown above, and is obtained, in purple crystals with a greenish luster, by evaporation of the solution. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially by passing ozone through the solution of the manganate: $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + O_2 + 2KOH$. **Sodium permanganate** $NaMnO_4$ is made in a similar manner. It is not obtainable in solid form, but its solution is known as "Condy's disinfecting fluid." This liquid owes its properties to the oxidizing power of the salt. **Permanganic acid** is a very active acid, that is, it is highly ionized in aqueous solution. A solid hydrate of the acid may be secured in reddish-brown crystals by adding sulphuric acid to a solution of barium permanganate and allowing the filtrate to evaporate:

$$Ba(MnO_4)_2 + H_2SO_4 + xH_2O \rightleftarrows BaSO_4 \downarrow + 2HMnO_4,xH_2O.$$

This hydrate decomposes, on being warmed to 32°, and yields oxygen and manganese dioxide. When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brownish-green, oily drops of **permanganic anhydride** (manganese heptoxide) Mn_2O_7 are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating-gas are set on fire by contact with it.

Potassium Permanganate as an Oxidizing Agent. — The actions are different according as the substance is employed (1) in acid, or (2) in neutral solution.

1. In presence of an acid, and an oxidizable body, a manganous salt is always formed. The schematic equation, $Mn_2O_7 \rightarrow 2MnO + 5O$, shows that every two molecules of the permanganate yield 5O for oxidizing purposes. Thus, when sulphuric acid is added to potassium permanganate solution, and sulphur dioxide is led through the mixture, we have:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O(+5O) \quad (1)$$
$$(5O) + 5H_2SO_3 \rightarrow 5H_2SO_4 \quad (2)$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5H_2SO_4$$

In this case, since sulphuric acid is a product, the preliminary addition of the acid was superfluous. In other cases, the partial equation (1), showing the available 5O, remains the same, while the other partial equation varies with the substance being oxidized. Thus, with hydrogen sulphide as reducing agent, we have:

$$(O) + H_2S \rightarrow H_2O + S \quad \times 5 \quad (2')$$

and with ferrous sulphate, we get ferric sulphate:

$$2FeSO_4 + H_2SO_4(+ O) \rightarrow Fe_2(SO_4)_3 + H_2O \quad \times 5 \quad (2'')$$

As before (2′) and (2″) must be multiplied throughout by five, before summation is made.

2. When dry potassium permanganate is heated, it decomposes as follows:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

The neutral solution oxidizes substances which are reducing agents. The fingers are stained brown by an aqueous solution, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar action. When the powdered salt is moistened with glycerine, the mass presently bursts into flame.

Analytical Reactions of Manganese Compounds — The ions commonly encountered are manganous-ion $Mn^{\cdot\cdot}$, which is very pale-pink in color, permanganate-ion MnO_4', which is purple, and man-

ganate-ion MnO_4'', which is green. The manganous compounds give with ammonium sulphide the flesh-colored, hydrated sulphide which is soluble in acids. Bases give the white hydroxide, which darkens by oxidation, and is soluble in salts of ammonium. All compounds of manganese confer upon the borax bead an amethyst color which, in the reducing flame, disappears. A bead of sodium carbonate and niter becomes green on account of the formation of the manganate.

Exercises. — 1. What do we mean by saying that, (*a*) chromous chloride is stable (p. 81), but easily oxidized by the air, (*b*) permanganic acid is an active oxidizing agent in presence of an acid (p. 194).

2. Formulate the oxidations of hydrogen sulphide, of ferrous sulphate, of oxalic acid (to carbon dioxide), and of nitrous acid (to nitric acid) by potassium permanganate in acid solution.

CHAPTER XLIII

IRON, COBALT, NICKEL

THE elements **iron** (Fe, at. wt. 55.9), **cobalt** (Co, at. wt. 59), and **nickel** (Ni, at. wt. 58.7) are not corresponding members of successive periods, like the families hitherto considered. They are neighboring members of the first long period, lying between its first and second octaves.

IRON Fe.

Chemical Relations of the Element. — The oxides and hydroxides FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$ are basic, the former more strongly so than the latter. The ferrous salts, derived from $Fe(OH)_2$, resemble those of the magnesium group and those of $Cr^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$, and are little hydrolyzed. The ferric salts, derived from $Fe(OH)_3$, resemble those of $Cr^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ and are hydrolyzed to a considerable extent. Iron gives also a few **ferrates** K_2FeO_4, $CaFeO_4$, etc., derived from an acid H_2FeO_4 which, like manganic acid H_2MnO_4 (p. 491), is too unstable to be isolated. Complex anions containing this element, such as the anion of $K_4.Fe(CN)_6$, are familiar, but complex cations containing ammonia are unknown.

Occurrence. — Free iron is found in minute particles in some basalts, and many meteorites are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3–8 per cent of nickel. The chief ores of iron are the oxides, hæmatite Fe_2O_3 and magnetite Fe_3O_4, and the carbonate $FeCO_3$, siderite. The first is reddish and radiated in structure; but black, shining, rhombohedral crystals, known as specularite, are also found. Hydrated forms, like brown iron ore $2Fe_2O_3, 3H_2O$, are also common. Siderite is pale-brown in color and rhombohedral, like calcite. When mixed with clay it forms iron-stone. Pyrite FeS_2 consists of golden-yellow, shining cubes or pentagonal dodecahedra. It is used, on account of its sulphur, in the manufacture of sulphuric

acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are contained in chlorophyll and in the blood (hæmoglobin), and doubtless play an important part in connection with the vital functions of these substances. Ammonium sulphide blackens the skin, forming ferrous sulphide by interaction with organic compounds of iron present in the tissues.

Metallurgy. — The ores of iron are first roasted in order to decompose carbonates and oxidize sulphides, if these salts are present. Coke is then used to reduce the oxides. Ores containing lime or magnesia are mixed with an acid flux, such as sand or clay-slate, in order that a fusible slag may be formed. Conversely, ores containing silica and clay are mixed with limestone. With proper adjustment of the ingredients the process can be carried on *continuously* in a blast furnace (Fig. 66). The solid materials thrown in at the top are converted, as they slowly descend, completely into gases which escape and liquids (iron and slag) which are tapped off at the bottom. Heated air is blown in at the bottom through tuyères, and the top is closed by a bell which descends for a moment when an addition is made to the charge. The gases, which contain much carbon monoxide, are led off and used to heat the blast or to drive gas-engines.

FIG. 66.

The main action takes place between the carbon monoxide, present in consequence of the excess of carbon, and the oxide of iron:

$$Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2.$$

Since the action is a reversible one, a large excess of carbon monoxide is required.

In the upper part of the furnace, the heat (400°) loosens the texture of the ore. Further down, the temperature is higher (500–

900°), and the carbon monoxide reduces the oxide of iron to particles of soft iron. A temperature high enough to melt pure iron is barely reached anywhere in the furnace, but, a little lower down, by union with carbon, the more fusible cast iron (1200°) is formed and falls in drops to the bottom. It is in this region also that the slag is produced. If the flux had begun sooner to interact with the unreduced ore, iron would have been lost by the formation of the silicate. The iron collects below the slag, and the latter flows continuously from a small hole. The former is tapped off at intervals of six hours or so from a lower opening.

Pure iron may be made by reducing the purified oxalate in a stream of hydrogen, or by Goldschmidt's method (p. 444).

Cast Iron and Wrought Iron. — Pure iron is not manufactured, and indeed would be too soft for most purposes. Piano-wire, however, is about 99.7 per cent pure. The product obtained from the blast furnace contains 92–94 per cent of iron along with 2.6–4.3 per cent of carbon, often nearly as much silicon, varying proportions of manganese, and some phosphorus and sulphur. The last four ingredients are liberated from combination with oxygen by the carbon in the hottest part of the furnace and combine or alloy themselves with the iron. Cast iron does not soften before melting, as does the purer wrought iron, but melts sharply at 1150–1250° according to the amount of foreign material it contains. When *suddenly* cooled it gives **chilled cast iron** which is very brittle and looks homogeneous to the eye, all the carbon being present in the form of carbide of iron Fe_3C in solid solution in the metal. This solid solution is exceedingly hard. By slower cooling, time is permitted for the separation of part of the carbon as graphite, which appears in tiny black scales, and **gray cast iron** results. This mixture is much softer, on account of the amount of free, relatively pure iron which it contains. **Spiegel iron** is cast iron made from ores containing 5–20 per cent of manganese and the usual proportion of carbon.

Wrought iron is made by heating the broken "pigs" of cast iron upon a layer of material containing oxide of iron and hammer-slag (basic silicate of iron) spread on the bed of a reverberatory furnace. The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and the last two pass into the slag. The sulphur is found in the slag as ferrous sulphide. On account of the effervescence due

to the escape of carbon monoxide, the process is called " pig-boiling." The iron is stirred with iron rods (" puddled ") and stiffens as it becomes purer, until finally it can be withdrawn in balls (" blooms ") and freed from slag under the steam-hammer or by rolling. It now softens sufficiently for welding below 1000° and melts at 1550°. Wrought iron should not contain more than 0.15 per cent of carbon. The above operations are now largely performed by machinery.

Steel. — This is a variety of iron almost free from phosphorus, sulphur, and silicon. Tool-steel contains 0.9–1.5 per cent of carbon, structural steel only 0.2–0.6 per cent, and mild steel 0.2 per cent or even less. Steel combines the properties of cast and of wrought iron, being hard and elastic, and at the same time available for forging and welding when the proportion of carbon is not too high.

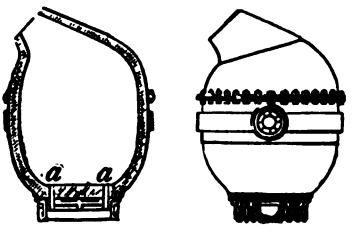


FIG. 67.

Steel is made largely by the **Bessemer process.** The molten cast iron is poured into a converter (Fig. 67) and a blast of air (*a*) is blown through it. The oxidation of the manganese, carbon, silicon, and a little of the iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carbon is then introduced by adding pure cast iron, spiegel iron, or coke, and the contents, first the slag, and then the molten steel, are finally poured out by turning the converter. When the cast iron contains much phosphorus, the oxide of this element is reduced again by the iron as fast as it is formed by the blast. In such cases a basic lining containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the Thomas-Gilchrist process. The slag (" Thomas-slag ") when pulverized forms a valuable fertilizer (*cf.* p. 401).

In the **Siemens-Martin,** or **open hearth** process, the cast iron is melted in a saucer-shaped depression lined with sand, and scraps of iron plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials are heated with

gas fuel for 8–10 hours until a sample shows, under the hammer, t the process is complete. The product is then drawn off throug hole and cast in molds.

When steel is heated to redness and cooled slowly, it is comp tively soft. Sudden chilling, however, renders it harder than gl The explanation of this behavior is the same as is the case of c iron (p. 496). By subsequent, cautious heating the hardness n be reduced to any required extent, and this treatment is ca "tempering."

Chemical Properties.—When exposed to moist air, iron recei a loosely adherent coating of rust ($2Fe_2O_3 \cdot Fe_2(OH)_6$). This prod may be formed by displacement of the hydrogen of carbo acid, the oxygen assisting (*cf.* p. 415), and subsequent hydrolysis the carbonate and oxidation of the ferrous hydroxide. The fa that alkalies prevent rusting favors this view, for they sho diminish the amount of hydrogen-ion. Many chemists belie however, that carbonic acid plays no part in the process.

Iron burns in oxygen and it interacts with superheated stea in both cases giving Fe_3O_4. A superficial layer of this oxide a heres firmly and protects the iron from the action of the air (Bar process for prevention of rusting).

Iron displaces hydrogen easily from dilute acids. Steel and ca iron, which contain iron, its carbide, and graphite, give with d dilute acids almost pure hydrogen, and the carbide and graphi remain unattacked. More concentrated acids, however, particula when warm, generate, along with hydrogen, hydrocarbons formed b interaction with the carbide (p. 330). The odor of the gas is due t compounds of sulphur and phosphorus.

Ferrous Compounds.—**Ferrous chloride** is obtained as a pale green hydrate $FeCl_2 \cdot 4H_2O$ by interaction of hydrochloric acid wit the metal or the carbonate. The anhydrous salt sublimes in colo less crystals when hydrogen chloride is led over the heated metal In solution the salt is oxidized by the air to a basic ferric chloride

$$4Fe^{\cdot\cdot} + O_2 + 2H_2O \rightarrow 4Fe^{\cdot\cdot\cdot} + 4OH'.$$

In presence of excess of the acid, normal ferric chloride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 295).

Ferrous hydroxide $Fe(OH)_2$ is thrown down as a white precipitate, but rapidly becomes dirty-green and finally brown, by oxidation. It dissolves in solutions of salts of ammonium, being, like magnesium hydroxide (p. 429), sufficiently soluble in water to require an appreciable concentration of OH' for its precipitation. The ammonium salts convert this into molecular ammonium hydroxide. **Ferrous oxide** FeO is black, and is formed by heating ferrous oxalate in absence of air. It may be made also by cautious reduction of ferric oxide by hydrogen (at about 300°), but is easily reduced further to the metal. It catches fire spontaneously when exposed to the air.

Ferrous carbonate $FeCO_3$ is found in nature, and may be made in slightly hydrolyzed form by precipitation. The precipitate is white but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid, after the manner of calcium carbonate (p. 324), and hence is found in solution in natural (chalybeate) waters.

Ferrous sulphide FeS may be formed as a black, metallic-looking mass by heating together the free elements. It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids. The precipitated form is slowly oxidized to ferrous sulphate by the air.

Ferrous sulphate is obtained by allowing pyrites to oxidize in the air and leaching the residue:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$

The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate $FeSO_4,7H_2O$, green vitriol, or "copperas," is deposited. The crystals are efflorescent, and become also brown from oxidation to a basic ferric sulphate:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4.$$

With excess of sulphuric acid and air, or an oxidizing agent, such as nitric acid, ferric sulphate is formed. The ferrous sulphate is used in dyeing and in making **writing-ink**. The extract of nut-galls contains tannic acid, $HC_{14}H_9O_9$, which, with ferrous sulphate, gives ferrous tannate. A solution of this salt containing gum-arabic and some dark coloring matter constitutes the ink. When the

writing is exposed to the air, the ferrous tannate is oxidized to the ferric condition, and the ferric compound is a fine, black precipitate (*cf.* p. 420).

Ferric Compounds. — By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent hydrate of **ferric chloride**, $FeCl_3$, $6H_2O$ is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, the anhydrous salt sublimes in dark scales, which are red by transmitted light. In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron. The same reduction is effected by hydrogen sulphide:

$$2Fe^{\cdot\cdot\cdot} + Fe \rightarrow 3Fe^{\cdot\cdot}.$$
$$2Fe^{\cdot\cdot\cdot} + S'' \rightarrow 2Fe^{\cdot\cdot} + S \downarrow.$$

The ferric ion is almost colorless, the yellow-brown color of solutions of ferric chloride being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated, and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand.

Ferric hydroxide $Fe(OH)_3$ appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this form the substance dries to the oxide without giving definite intermediate hydrated oxides. The hydrates, $Fe_2O_3,2Fe(OH)_3$ (brown iron ore) and $Fe_2O_3,4Fe(OH)_3$ (bog iron ore), however, are found in nature (see Rust, p. 498). The hydroxide passes easily into colloidal solution in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment the salt can be separated, and a pure aqueous solution of the hydroxide obtained. This solution is red in color, shows no depression in the freezing-point, and is not an electrolyte. It deposits the hydroxide as a brown precipitate when various substances are added to the solution.

Ferric oxide, Fe_2O_3, is sold as " rouge " and " Venetian red." It is made from the ferrous sulphate, obtained in cleaning iron ware which is to be tinned or galvanized, and in other ways in the arts. The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite

$Zn(FeO_2)_2$ may be formed. It is reduced by hydrogen, at about 300° to ferrous oxide (p. 499), and at 700–800° to metallic iron.

Magnetic oxide of iron Fe_3O_4 or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals.

Ferric sulphide Fe_2S_3 may be made by fusing together the free elements, but is not obtained by precipitation. Soluble sulphides first reduce the ferric salt to the ferrous conditions, liberating sulphur,

$$Fe_2(SO_4)_3 + (NH_4)_2S \rightarrow 2FeSO_4 + (NH_4)_2SO_4 + S,$$

and then give ferrous sulphide (p. 254).

Ferric sulphate $Fe_2(SO_4)_3$ is formed by oxidation of ferrous sulphate, and is obtained as a white mass by evaporation. It gives alums, such as $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, which are almost colorless when pure, but usually have a pale reddish-violet tinge.

Pyrite. — The mineral pyrite FeS_2 (Fools' gold) is the sulphide of iron which is most stable in the air. It is found in nature in the form of glittering, golden-yellow cubes, octahedrons, and pentagonal dodecahedrons. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur. It is reduced by hydrogen to ferrous sulphide.

Cyanides. — When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides of the forms $4KCN,Fe(CN)_2$ and $3KCN,Fe(CN)_3$. These are called ferro- and ferricyanide of potassium, respectively.

Ferrocyanide of potassium $K_4Fe(CN)_6, 3H_2O$, "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:

$$2KCN + FeS \rightarrow Fe(CN)_2 + K_2S,$$
$$4KCN + Fe(CN)_2 \rightarrow K_4.Fe(CN)_6.$$

The salt is made also from the cyanogen contained in crude illuminating-gas. The trihydrate forms large, yellow, monosymmetric tables. The solution contains almost exclusively the ions $K^{\cdot}$ and

$Fe(CN)_6''''$, and gives none of the reactions of the ferrous ion $Fe^{\cdot\cdot}$. The corresponding acid $H_4.Fe(CN)_6$ may be obtained as white crystalline scales by addition of an acid and of ether (in which the substance is less soluble than in water) to the salt. The acid is a fairly active one, but is unstable and decomposes in a complex manner. Other ferrocyanides may be made by precipitation. That of copper $Cu_2.Fe(CN)_6$ is brown, and ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ has a brilliant blue color ("Prussian blue"). The ferrous compound $Fe_2Fe(CN)_6$, or perhaps $K_2FeFe(CN)_6$, is white but quickly becomes blue by oxidation. The ferrocyanides are not poisonous.

Ferricyanide of potassium $K_3Fe(CN)_6$ is easily made from the ferrocyanide by oxidation:

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2KCl + 2K_3.Fe(CN)_6,$$

or

$$2Fe(CN)_6'''' + Cl_2 \rightarrow 2Fe(CN)_6''' + 2Cl'.$$

It forms red monosymmetric prisms. The free acid $H_3Fe(CN)_6$ is unstable. Other salts may be prepared by precipitation. Ferrous ferricyanide $Fe_3[Fe(CN)_6]_2$ is deep-blue in color ("Turnbull's blue"). With ferric salts only a brown solution is obtained.

Iron Carbonyls. — When carbon monoxide is led over finely divided iron at 40–80°, or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition $Fe(CO)_4$, the tetracarbonyl, and $Fe(CO)_5$, the pentacarbonyl, are formed. When the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

Analytical Reactions of Compounds of Iron. — There are two ionic forms of iron, ferrous-ion $Fe^{\cdot\cdot}$, which is very pale-green, and ferric-ion $Fe^{\cdot\cdot\cdot}$, which is almost colorless. Ammonium sulphide forms, with both, black ferrous sulphide which is soluble in dilute acids. The hydroxides are white and brown respectively, and ferrous carbonate is white. With ferric salts, soluble carbonates yield the hydroxide. With ferrocyanide of potassium, ferrous salts give a white, and ferric salts a blue, precipitate. With ferricyanide of potassium the former give a deep-blue precipitate, and the latter a brown solution. **Ferric thiocyanate** $Fe(CNS)_3$ is deep-red (p. 179).

With borax, iron compounds give a bead which is green in the reducing flame, and colorless or, with much iron, yellow or even brown when oxidized.

Cobalt Co.

The Chemical Relations of the Element. — Cobalt forms cobaltous and cobaltic oxides and hydroxides CoO and $Co(OH)_2$, Co_2O_3 and $Co(OH)_3$, respectively, which are all basic, the former more so than the latter. The cobaltous salts are little hydrolyzed, but the cobaltic salts are completely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.

Occurrence and Properties. — Cobalt is found along with nickel in smaltite $CoAs_2$ and cobaltite CoAsS. The pure metal may be made by Goldschmidt's process, or by reducing the oxalate, or an oxide, with hydrogen.

The metal is silver-white, with a faint suggestion of pink. It is less tough than iron, and has no commercial applications. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

Cobaltous Compounds. — The **chloride** $CoCl_2, 6H_2O$ may be made by treating the oxide with hydrochloric acid. It forms red prisms, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the air, and is once more invisible (" sympathetic ink "). Most cobaltous compounds are red when hydrated or in solution ($Co^{\cdot\cdot}$) and blue when dehydrated. By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the red **cobaltous hydroxide**, $Co(OH)_2$ is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide, which is quickly oxidized by the air to an ammonio-cobaltic compound (see below). It dissolves also in salts of ammonium as magnesium hydroxide does (p. 429). When dehydrated it leaves the black **cobaltous oxide** CoO. **Cobaltous sulphate**, $CoSO_4, 7H_2O$,

and **cobaltous nitrate**, $Co(NO_3)_2$, $6H_2O$, are familiar salts. The black **cobaltous sulphide**, CoS, is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the acetate, or a solution containing much sodium acetate (*cf.* p. 399). Once it has been formed, it does not interact even with dilute hydrochloric acid, having apparently changed into a less active form. A sort of **cobalt glass**, made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment (" smalt ") used in china-painting and by artists.

Cobaltic Compounds. — By addition of a hypochlorite to a solution of a cobaltous salt, **cobaltic hydroxide** $Co(OH)_3$, a black powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide**, Co_2O_3. Stronger ignition gives the commercial oxide, which is a **cobalto-cobaltic oxide** Co_3O_4. Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed. By placing cobaltous sulphate round the anode of an electrolytic cell, crystals of **cobaltic sulphate**, $Co_2(SO_4)_3$, have been made and cobaltic alums have also been prepared.

Complex Compounds. — Potassium cyanide precipitates from cobaltous salts a brownish-white cyanide which interacts with excess of the reagent, giving a solution of **potassium cobaltocyanide** $K_4.Co(CN)_6$ (*cf.* p. 501). This compound is easily oxidized by chlorine, or even when the solution is boiled in the air, and the colorless **potassium cobalticyanide** is formed:

$$4K_4Co(CN)_6 + 2H_2O + O_2 \rightarrow 4K_3.Co(CN)_6 + 4KOH.$$

The solution gives none of the reactions of $Co^{\cdot\cdot\cdot}$, and with acids the very stable cobalticyanic acid, $H_3Co(CN)_3$, is liberated.

When acetic acid and potassium nitrite are added to a cobaltous salt, the latter is oxidized by the nitrous acid (liberated by the acetic acid) and a white complex salt $K_3.Co(NO_2)_6,nH_2O$ ($= Co(NO_2)_3, 3KNO_2$), **potassium cobaltinitrite**, is thrown down.

Cobaltic salts give with ammonia complex compounds which are many and various. The cations often contain negative groups, and are such as $Co(NH_3)_6^{\cdot\cdot\cdot}$, $Co(NH_3)_5Cl^{\cdot\cdot}$ and $Co(NH_3)_5NO_2^{\cdot\cdot}$. Usually the solutions give none of the reactions of cobaltic ions, and often fail likewise to give those of the anion of the original salt.

NICKEL.

The Chemical Relations of the Element. — Nickel forms nickelous and nickelic oxides and hydroxides NiO and $Ni(OH)_2$, Ni_2O_3, and $Ni(OH)_3$, but only the former are basic. The nickelous salts resemble the cobaltous and ferrous salts, but are not oxidizable into corresponding nickelic compounds. Since there are no nickelic salts, there are here no analogues of the cobalticyanides or the cobaltinitrites. The complex nickelous salts, like the complex cobaltous salts, and unlike the complex cobaltic salts, are unstable, and so give some of the reactions of $Ni^{\cdot\cdot}$.

Occurrence and Properties. — Nickel occurs free in meteorites and in niccolite NiAs and nickel glance NiAsS. It is now manufactured chiefly from pentlandite [Ni,Fe]S and other minerals found at Sudbury (Ontario), and from garnierite, a silicate of nickel and magnesium found in New Caledonia.

The metal is white, with a faint tinge of yellow, is very hard, and takes a high polish. It is used in making alloys, such as German silver (copper, zinc, nickel, 2 : 1 : 1) and the " nickel " used in coinage (copper, nickel, 3 : 1). Nickel plating on iron is accomplished exactly like silver plating (p. 421). The bath contains an ammoniacal solution of ammonium-nickel sulphate $(NH_4)_2SO_4,NiSO_4, 6H_2O$, and a plate of nickel forms the anode.

The metal rusts very slowly in moist air. It displaces hydrogen with difficulty from dilute acids but interacts with nitric acid.

Compounds of Nickel. — The **chloride** $NiCl_2,6H_2O$, is made by treating any of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The **sulphate**, $NiSO_4,6H_2O$, which crystallizes in square prismatic forms at 30–40°, is the most familiar salt. **Nickelous hydroxide**, $Ni(OH)_2$, is formed as an apple-green precipitate, and when heated leaves the green **nickelous oxide**, NiO. It dissolves in ammonium hydroxide, giving a complex nickel-ammonia cation. It is soluble also in salts of ammonium (*cf.* p. 429). By cautious ignition of the nitrate, **nickelic oxide**, Ni_2O_3, is formed as a black powder. The oxides and salts, when heated strongly in oxygen give the oxide Ni_3O_4. The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. **Nickelic hydroxide**, $Ni(OH)_3$, is a black precipitate formed when a

hypochlorite is added to any salt of nickel. **Nickelous sulphide** is thrown down by ammonium sulphide, and behaves like cobaltous sulphide (p. 504). It forms a brown colloidal solution when excess of the precipitant is used, and is then deposited very slowly.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide**, $Ni(CN)_2$, is first precipitated. This dissolves in excess of the reagent, and a complex salt $K_2Ni(CN)_4$, H_2O ($= 2KCN,Ni(CN)_2$) may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and of iron, and is less stable. Thus, with bleaching powder, it gives $Ni(OH)_3$ as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelicyanide occurs, and indeed no such salts are known. This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalticyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. The only known compound which could be formed, $4KNO_2,Ni(NO_2)_2$, is soluble. This action also is used for the purpose of separation.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, **nickel carbonyl** $Ni(CO)_4$ is formed. This is a vapor and is condensable to a colorless liquid (b.-p. 43° and m.-p. − 25°). The vapor is poisonous. When heated to 150–180° it is dissociated and nickel is deposited. Cobalt forms no corresponding compound.

Analytical Reactions of Compounds of Cobalt and Nickel. — The cobalt ion $Co^{\cdot\cdot}$ is pink, and the nickelous ion $Ni^{\cdot\cdot}$ green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead, and nickel compounds a bead which is brown in the oxidizing flame and cloudy, from the presence of gray, metallic nickel, when reduced.

Exercises.— 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing, (*a*) the oxidation of ferrous chloride by air, (*b*) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (*c*) the oxidation of ferrous sulphate

with excess of sulphuric acid by hypochlorous acid, (*d*) the formation of ferrous and ferric tannates (p. 499), (*e*) the reduction of ferric chloride by iron and by hydrogen sulphide, respectively, (*f*) the dry distillation of basic ferric sulphate, (*g*) the formation of ferric ferrocyanide and of ferrous ferricyanide.

3. Explain the solubility of cobaltous and nickelous hydroxide in salts of ammonium.

4. Construct equations to show the formation, (*a*) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (*b*) of nickelic hydroxide from nickelous chloride and sodium hypochlorite.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, with especial reference to showing the resemblances and differences.

Platinum.—This metal (dim. of Sp. *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame but fuses easily in the oxyhydrogen jet. On account of its very small chemical activity it is used in electrical apparatus and for making wire, foil, and crucibles and other vessels for use in laboratories. It interacts with fused alkalies, giving platinates. The oxygen acids are without action upon it, but the free chlorine in *aqua regia* converts it into chloroplatinic acid H_2PtCl_6.

The metal condenses oxygen upon its surface and it dissolves hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate $(NH_4)_2PtCl_6$, and **platinum black** made by adding zinc to chloroplatinic acid, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequence of the heat developed by the rapid union of that part of the gases which is condensed in the metal. A heated spiral of fine platinum wire will continue to glow if immersed in the mixture of alcohol vapor and oxygen formed by leading oxygen through liquid alcohol. The heat is developed by the interaction which takes place between the substances with great speed at the surface of the platinum. Platinum sponge is the active constituent of the contact-mass used in making sulphur trioxide (p. 257).

Platinum is the only otherwise suitable substance which has the same coefficient of expansion as glass, and it is consequently fused into incandescent bulbs and furnishes the electrical connection with the filament in the interior. Large amounts are also consumed in photography. The price of the metal is subject to great variations, since a rainy season in the Caucasus will render larger amounts accessible to the miners; but, on the whole, the many applications which have been found for it have tripled its price in the last twenty years.

When special resistance to chemical or mechanical influences is required, as in standard meters for international reference, or points of fountain pens, the alloy with iridium is employed.

Compounds of Platinum.—**Platinous chloride** is made by passing chlorine over finely divided platinum at 240–250° or by heating chloroplatinic acid to the same temperature. It is greenish and

insoluble in water, but forms with hydrochloric acid the soluble **chloroplatinous acid** H_2PtCl_4. Potassium chloroplatinite K_2PtCl_4 is used in making platinum prints. Bases precipitate black **platinous hydroxide** $Pt(OH)_2$ which interacts with acids but not with bases. Gentle heating gives the **oxide** PtO and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platino-cyanides**, $K_2Pt(CN)_4,3H_2O$ and $BaPt(CN)_4,4H_2O$, are formed. These substances, when solid, show strong fluorescence, converting X-rays as well as ultra-violet rays into visible radiations. The barium salt is used to coat screens on which the shadows cast by X-rays are received.

Chloroplatinic acid $H_2PtCl_6,6H_2O$ is made by treating the metal with *aqua regia*, and forms reddish-brown deliquescent crystals. With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates K_2PtCl_6 and $(NH_4)_2PtCl_6$ (*cf.* p. 369), in solutions of which the platinum migrates towards the anode and silver salts precipitate Ag_2PtCl_6 and not silver chloride. Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide** $Pt(OH)_4$. This substance interacts with bases to give **platinates**, like $Na_2H_{10}Pt_3O_{12},H_2O$. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides**, PtS and PtS_2 respectively. These are black powders which dissolve in yellow ammonium sulphide solution, much as do the sulphides of gold, arsenic, and other metals, giving ammonium sulphoplatinates.

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[redacted]

E^0	E^ICl E_2^IO	$E^{II}Cl_2$ $E^{II}O$	[illegible]
He = 4 Ne = 20	Li = 7 Na = 23	Gl = 9 Mg = 24.4	
A = 39.9	K = 39 Cu = 63.6	Ca = 40 Zn = 65.4	Sc [illegible]
Kr = 87.8	Rb = 85.4 Ag = 108	Sr = 87.6 Cd = 112.4	Y = [illegible]
X = 128	Cs = 133 Au = 197	Ba = 137.4 Hg = 200	La [illegible]
. . . .	. . .	Ra = 226.5	. . .

In this table atomic weights are giv[illegible]

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ELEMENTS	SYMBOLS	AT. WT. O = 16	ELEMENTS	SYMBOLS	AT. WT. O = 16
Aluminium	Al	27.1	Neodymium	Nd	143.6
Antimony	Sb	120.2	Neon	Ne	20.
Argon	A	39.9	Nickel	Ni	58.7
Arsenic	As	75.0	Nitrogen	N	14.01
Barium	Ba	137.4	Osmium	Os	191.0
Bismuth	Bi	208.0	Oxygen	O	16.00
Boron					
Bromine					
Cadmium					
Caesium					
Calcium					
Carbon					
Cerium					
Chlorine					
Chromium					
Cobalt					
Columbium					
Copper					
Erbium					
Fluorine					
Gadolinium					
Gallium					
Germanium					
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